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(54) **Black magnetic composite particles and black magnetic toner using the same**

(57) Black magnetic composite particles for a black magnetic toner comprising:

(a) magnetic iron oxide particles having an average particle diameter of from 0.055 to 0.95 μm;
(b) a coating on the surface of said magnetic iron oxide particles, comprising at least one organosilicon compound selected from:

(1) organosilane compounds obtainable by drying or heat-treating alkoxysilane compounds,
(2) polysiloxanes or modified polysiloxanes, and
(3) fluoroalkyl organosilane compounds obtainable by drying or heat-treating fluoroalkylsilane compounds; and

(c) carbon black fine particles adhered on at least a part of said coating, which have a particle size of from 0.002 to 0.05 μm and which are present in an amount of from 1 to 25 parts by weight per 100 parts by weight of said magnetic iron oxide particles.

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Descripti n

[0001] Th present invention relates to black magnetic composit particles and a black magnetic toner, and more particularly, to black magnetic composite particles for black magnetic toner which not only show an exc llent disp rsibility in a binder resin due to less amount of carbon black fine particles fallen-off from the surface of each particle, but also have an excellent fluidity and blackness, and a black magnetic toner using such black magnetic composite particles.

[0002] As one of conventional electrostatic latent image-developing methods, there has been widely known and generally adopted a so-called one component system development method of using as a developer, a magnetic toner comprising composite particles prepared by mixing and dispersing magnetic particles such as magnetite particles in a resin, without using a carrier.

[0003] The conventional development methods of using one-component magnetic toner have been classified into CPC development methods of using a low-resistance magnetic toner, and PPC development methods of using a high-resistance magnetic toner.

[0004] In the CPC methods, the low-resistance magnetic toner used therefor has an electric conductivity, and is charged by the electrostatic induction due to electric charge of the latent images. However, since the charge induced on the magnetic toner is lost while the magnetic toner is transported from a developing zone to a transfer zone, the low-resistance magnetic toner is unsuitable for the PPC development method of using an electrostatic transfer method. In order to solve this problem, there have been developed the insulated or high resistance magnetic toners having a volume resistivity as high as not less than 10^{14} Ω·cm.

[0005] As to the insulated or high-resistance magnetic toner, it is known that the developing characteristics thereof are affected by magnetic particles exposed to the surface of the magnetic toner, or the like.

[0006] Recently, with the high image quality such as high image density or high tone gradation, or with the high copying speed of duplicating machines, it has been strongly demanded to further enhance characteristics of the insulted or high-resistance magnetic toners as a developer, especially a fluidity thereof.

[0007] With respect to such demands, in Japanese Patent Application Laid-Open (KOKAI) No. 53-94932(1978), there has been described "these high-resistance magnetic toners are deteriorated in fluidity due to the high electric resistance, so that there arises such a problem that non-uniformity of developed images tend to be caused. Namely, although the high-resistance magnetic toners for PPC development method can maintain necessary charges required for image transfer, the magnetic toners are frictionally charged even when they are present in other steps than the transfer step, where the magnetic toners are not required to be charged, e.g., in a toner bottle or on the surface of a magnetic roll, or also slightly charged by mechano-electrets during the production process of these magnetic toners. Therefore, the magnetic toners tend to be electrostatically agglomerated, resulting in deterioration of fluidity thereof", and "It is an another object of the present invention to provide a high-resistance magnetic toner for PPC development method which is improved in fluidity, can be prevented from causing non-uniformity of developed images, and has an excellent image definition and tone gradation, thereby obtaining high-quality copies by indirect copying methods".

[0008] In recent years, with the reduction in particle size of the insulated or high-resistance magnetic toners, it has been increasingly required to enhance the fluidity thereof.

[0009] With respect to such a fact, in "Comprehensive Data Collection for Development and Utilization of Toner Materials" published by Japan Scientific Information Co., Ltd., page 121, there has been described "With extensive development of printers such as ICP, a high image quality has been required. In particular, it has been demanded to develop high-precision or high-definition printers. In Table 1, there is shown a relationship between definitions obtained by using the respective toners. As is apparent from Table 1, the smaller the particle size of wet toners, the higher the image definition is obtained. Therefore, when a dry toner is used, in order to enhance the image definition, it is also required to reduce the particle size of the toner .... As reports of using toners having a small particle size, it has been proposed that by using toners having a particle size of 8.5 to 11 µm, fogs on a background can be improved and toner consumption can be reduced, and further by using polyester-based toners having a particle size of 6 to 10 µm, an image quality, a charging stability and lifetime of the developer can be improved. However, when such toners having a small particle size are used, it has been required to solve many problems. There are problems such as improvement in productivity, sharpness of particle size distribution, improvement in fluidity, etc.".

[0010] Further, black magnetic toners widely used at the present time, have been required to show a high degree of blackness and a high image density for line images and solid area images on copies.

[0011] With respect to this fact, on page 272 of the above-mentioned "Compreh nsiv Data Collection for Development and Utilization of Toner Materials", there has been described "Powder development is characterized by a high image density. How v r, th high image density as w ll as th fog d nsity as described her inafter, greatly influ nc s image characteristics obtained".

[0012] Ther is a close r lationship betw n prop rties of the magnetic ton r and thos of the magnetic particles mixed and dispersed in th magnetic toner.

[0013] That is, the fluidity of the magnetic ton r is largely varied depending upon surface condition of the magnetic particles expos d to the surfac of the magnetic toner. Therefore, th magnetic particl s thems lves have been strongly required to show an excellent fluidity.

[0014] The degr e of blackness and density of the magnetic toner are also largely varied depending upon th degre of blackness and density of the magnetic particles as a black pigment contained in the magnetic toner.

[0015] As the black pigment, magnetite particles have been widely used from the standpoints of magnetic properties such as saturation magnetization or coercive force, low price, color tone or the like. In addition to the magnetite particles, carbon black fine particles may be added. However, in the case where the carbon black fine particles are used in a large amount, the electric resistance is lowered, so that it is not possible to obtain an insulated or high-resistance magnetic toner.

[0016] Hitherto, in order to enhance the fluidity of the black magnetic toner, there have been many attempts of improving the fluidity of the magnetite particles mixed and dispersed in the magnetic toner. For example, there have been proposed (1) a method of forming spherical-shaped magnetite particles (Japanese Patent Application Laid-Open (KOKAI) No. 59-64852(1984)), (2) a method of exposing a silicon compound to the surface of magnetite particles (Japanese Patent Publication (KOKOKU) No. 8-25747(1996)), or the like.

[0017] Black magnetic particles for black magnetic toner, which have not only an excellent fluidity and blackness, but also an excellent dispersibility in a binder resin, are presently strongly demanded. However, black magnetic particles capable of satisfying all of these requirements have not been obtained yet.

[0018] Namely, the above-mentioned spherical magnetite particles show a higher fluidity than those of cubic magnetite particles, octahedral magnetite particles or the like. However, the fluidity of the spherical magnetite particles is still insufficient, and further the blackness is disadvantageously low.

[0019] As to the above-mentioned magnetite particles to the surface of which the silicon compound is exposed, the fluidity thereof is also still insufficient, and the blackness thereof is also disadvantageously low.

[0020] As a result of the present inventor's earnest studies for solving the above problems, it has been found that by coating magnetic iron oxide particles having an average particle size of 0.055 to 0.95 μm with an organosilicon compound, then adhering carbon black fine particles having an average particle size of 0.002 to 0.05 μm on a coating of the organosilicon compound to obtain black magnetic composite particles, a black magnetic toner produced by using the obtained black magnetic composite particles, can have not only an excellent fluidity and an excellent blackness, but also can show a high-resistance or an insulating property without lowering in the electric resistance. The present invention has been attained on the basis of the finding.

[0021] It is an object of the present invention to provide black magnetic particles for black magnetic toner, which are not only excellent in fluidity and blackness, but also can show an excellent dispersibility in a binder resin.

[0022] It is another object of the present invention to provide a black magnetic toner, which is not only excellent in fluidity and blackness, but also small in reduction of electric resistance and, therefore, can realize a high image quality and a high copying speed.

[0023] To accomplish the aims, in a first aspect of the present invention, there is provided black magnetic composite particles for a black magnetic toner, comprising:

magnetic iron oxide particles having an average particle diameter of 0.055 to 0.95 μm;
a coating formed on surface of said magnetic iron oxide particles, comprising at least one organosilicon compound selected from the group consisting of:

(1) organosilane compounds obtained by drying or heat-treating an alkoxysilane compounds,
(2) polysiloxanes or modified polysiloxanes, and
(3) fluoroalkyl organosilane compounds obtained by drying or heat-treating a fluoroalkylsilane compounds; and

carbon black fine particles adhered on at least a part of said coating, having a particle size of 0.002 to 0.05 μm, the amount of said carbon black fine particles adhered being 1 to 25 parts by weight based on 100 parts by weight of said magnetic iron oxide particles.

[0024] In a second aspect of the present invention, there is provided black magnetic composite particles for a black magnetic toner, comprising:

magnetic iron oxide particles having an average particle diameter of 0.055 to 0.95 μm, and having a coat which is formed on at least a part of the surfac of said magn tic iron oxide particles and which comprises at least one compound sel cted from the group consisting of hydroxides of aluminum, oxides of aluminum, hydroxid s of silicon and oxides of silicon in an amount of 0.01 to 50 % by w ight, calculated as Al or SiO_2, based on th total weight of the magnetic iron oxide particles;

a coating formed on surface of said magnetic iron oxide particles, comprising at l ast one organosilicon compound selected from the group consisting of:

(1) organosilane compounds obtained by drying or heat-treating an alkoxysilane compounds,
(2) polysiloxanes or modified polysiloxanes, and
(3) fluoroalkyl organosilane compounds obtained by drying or heat-treating a fluoroalkylsilane compounds; and

carbon black fine particles adhered on at least a part of said coating, having a particle size of 0.002 to 0.05 μm, the amount of said carbon black fine particles adhered being 1 to 25 parts by weight based on 100 parts by weight of said magnetic iron oxide particles.

[0025] In a third aspect of the present invention, there is provided black magnetic toner comprising:

said black magnetic composite particles comprising:
magnetic iron oxide particles having an average particle diameter of 0.055 to 0.95 μm;
a coating formed on surface of said magnetic iron oxide particles, comprising at least one organosilicon compound selected from the group consisting of:

(1) organosilane compounds obtained by drying or heat-treating an alkoxysilane compounds,
(2) polysiloxanes or modified polysiloxanes, and
(3) fluoroalkyl organosilane compounds obtained by drying or heat-treating a fluoroalkylsilane compounds; and

carbon black fine particles adhered on at least a part of said coating, having a particle size of 0.002 to 0.05 μm, the amount of said carbon black fine particles adhered being 1 to 25 parts by weight based on 100 parts by weight of said magnetic iron oxide particles, and
a binder resin.

[0026] In a fourth aspect of the present invention, there is provided black magnetic toner comprising:

said black magnetic composite particles comprising:
magnetic iron oxide particles having an average particle diameter of 0.055 to 0.95 μm, and having a coat which is formed on at least a part of the surface of said magnetic iron oxide particles and which comprises at least one compound selected from the group consisting of hydroxides of aluminum, oxides of aluminum, hydroxides of silicon and oxides of silicon in an amount of 0.01 to 50 % by weight, calculated as Al or SiO_2, based on the total weight of the magnetic iron oxide particles;
a coating formed on surface of said magnetic iron oxide particles, comprising at least one organosilicon compound selected from the group consisting of:

(1) organosilane compounds obtained by drying or heat-treating an alkoxysilane compounds,
(2) polysiloxanes or modified polysiloxanes, and
(3) fluoroalkyl organosilane compounds obtained by drying or heat-treating a fluoroalkylsilane compounds; and

carbon black fine particles adhered on at least a part of said coating, having a particle size of 0.002 to 0.05 μm, the amount of said carbon black fine particles adhered being 1 to 25 parts by weight based on 100 parts by weight of said magnetic iron oxide particles, and
a binder resin.

[0027] In a fifth aspect of the present invention, there is provided a method of using black magnetic composite particles for production of a black magnetic toner, which black magnetic composite particles comprise comprising:

magnetic iron oxide particles having an average particle diameter of 0.055 to 0.95 μm;
a coating formed on surface of said magnetic iron oxide particles, comprising at least one organosilicon compound selected from the group consisting of:

(1) organosilane compounds obtain d by drying or heat-tr ating an alkoxysilan compounds,
(2) polysiloxan s or modified polysiloxan s, and
(3) fluoroalkyl organosilane compounds obtain d by drying or heat-treating a fluoroalkylsilane compounds; and

carbon black fine particles adhered on at least a part of said coating, having a particle size of 0.002 to 0.05 μm, the amount of said carbon black fin particl s adhered b ing 1 to 25 parts by w ight based on 100 parts by w ight of said magnetic iron oxide particles.

In the accompanying drawings

[0028] Fig. 1 is an electron micrograph (× 20,000) showing a particle structure of spherical magnetite particles used in Example 1.

[0029] Fig. 2 is an electron micrograph (× 20,000) showing a particle structure of carbon black particles used in Example 1.

[0030] Fig. 3 is an electron micrograph (× 20,000) showing a particle structure of black magnetic composite particles obtained in Example 1.

[0031] Fig. 4 is an electron micrograph (× 20,000) showing a particle structure of mixed particles composed of the spherical magnetite particles and the carbon black fine particles, for comparative purpose.

[0032] The present invention is now described in detail below.

[0033] First, the black magnetic composite particles according to the present invention are described.

[0034] The black magnetic composite particles according to the present invention, comprise magnetic iron oxide particles as core particles having an average particle diameter of 0.055 to095 μm, a coating comprising an organosilicon compound which is formed on the surface of each magnetic iron oxide particle, and carbon black fine particles having an average particle size of 0.002 to 0.05 μm, adhered on at least a part of the coating comprising the organosilicon compound.

[0035] As the magnetic iron oxide particles used as core particles in the present invention, there may be exemplified magnetite particles ($FeO_x \cdot Fe_2O_3$; $0<X\leq 1$), maghemite particles (γ-Fe_2O_3) or a mixture of these particles. In the consideration of blackness of the obtained black magnetic composite particles, magnetite particles are preferred.

[0036] As the magnetic iron oxide particles as core particles, from the viewpoint of a particle shape thereof, there may be exemplified isotropic particles having a ratio of an average particle length (average major diameter) to an average particle breadth (average minor diameter) of usually not less than 1.0 and less than 2.0, preferably 1.0 to 1.8, more preferably 1.0 to 1.5, such as spherical particles, granular particles or polyhedral particles, e.g., hexahedral particles or octahedral particles, or anisotropic particles having an aspect ratio (average major axial diameter/average minor axial diameter; hereinafter referred to merely as "aspect ratio") of not less than 2:1, such as acicular particles, spindle-shaped particles or rice ball-shaped particles. In the consideration of the fluidity of the obtained black magnetic composite particles, the magnetic iron oxide particles having an isotropic shape are preferred. Among them, the spherical particles are more preferred.

[0037] In the case of the isotropic magnetic iron oxide particles, the average particle size (diameter) thereof is 0.055 to 0.95 μm, preferably 0.065 to 0.75 μm, more preferably 0.065 to 0.45 μm. In the case of the anisotropic magnetic iron oxide particles, the average major axial diameter thereof is 0.055 to 0.95 μm, preferably 0.065 to 0.75 μm, more preferably 0.065 to 0.45 μm, and the aspect ratio (average major axial diameter/average minor axial diameter) thereof is 2:1 to 20:1, preferably 2:1 to 15:1, more preferably 2:1 to 10:1.

[0038] When the average particle size of the magnetic iron oxide particles is more than 0.95 μm, the obtained black magnetic composite particles are coarse particles and are deteriorated in tinting strength. On the other hand, when the average particle size is less than 0.055 μm, the intermolecular force between the particles is increased due to the reduction in particle size (fine particle), so that agglomeration of the particles tends to be caused. As a result, it becomes difficult to uniformly coat the surfaces of the magnetic iron oxide particles with the organosilicon compounds, and uniformly adhere the carbon black fine particles on the surface of the coating comprising the organosilicon compounds.

[0039] Further, in the case where the upper limit of the aspect ratio of the anisotropic magnetic iron oxide particles exceeds 20:1, the particles tend to be entangled with each other, and it also becomes difficult to uniformly coat the surfaces of the magnetic iron oxide particles with the organosilicon compounds, and uniformly adhere the carbon black fine particles on the surface of the coating composed of the organosilicon compounds.

[0040] As to the particle size distribution of the magnetic iron oxide particles, the geometrical standard deviation value thereof is preferably not more than 2.0, more preferably not more than 1.8, still more preferably not more than 1.6. When the geometrical standard deviation value thereof is more than 2.0, coarse particles are contained therein, so that the particles are inhibited from being uniformly dispersed. As a result, it also becomes difficult to uniformly coat the surfac s of th magnetic iron oxide particles with th organ silicon compounds, and uniformly adh re the carbon black fine particles on the surface of the coating composed of the organosilicon compounds. The lower limit of th geometrical standard deviation value is 1.01. It is industrially difficult to obtain particles having a geometrical standard deviation value of less than 1.01.

[0041] The BET specific surfac area of the magn tic iron oxide particles there f is not less than 0.5 m²/g. Wh n the BET specific surfac area is l ss than 0.5 m²/g, the magn tic iron oxide particles may become coars particles,

or the sintering between the particles may be caused, so that the obtained black magnetic composit particles also may becom coarse particles and t nd to be deteriorated in tinting strength. In the consideration of the tinting strength of the obtain d black magnetic composite particles, th BET specific surfac area of the magnetic iron oxide particles is preferably not less than 1.0 m^2/g, more pref rably 3.0 m^2/g. Further, in the consideration of uniformly coating the surfaces of the magnetic iron oxide particles with the organosilicon compounds, and uniformly adhering the carbon black fine particles on a coating composed of the organosilicon compounds, the upper limit of the BET specific surface area of the magnetic iron oxide particles, is usually 70 m^2/g, preferably 50 m^2/g, more preferably 20 m^2/g.

[0042] As to the fluidity of the magnetic iron oxide particles, the fluidity index thereof is about 25 to about 44. Among the magnetic iron oxide particles having various shapes, the spherical particles are excellent in fluidity, for example, the fluidity index thereof is about 30 to about 44.

[0043] As to the blackness of the magnetic iron oxide particles, in the case of the magnetite particles, the lower limit thereof is usually 18.0 when represented by L* value, and the upper limit thereof is usually 25.0, preferably 24.0 when represented by L* value. In the case of maghemite particles, the lower limit thereof is usually more than 18.0 when represented by L* value, and the upper limit thereof is usually 32, preferably 30 when represented by L* value. When the L* value exceeds the above-mentioned upper limit, the lightness of the particles is increased, so that it is difficult to obtain black magnetic composite particles having a sufficient blackness.

[0044] As to the magnetic properties of the magnetic iron oxide particles, the coercive force value thereof is usually about 10 to about 350 Oe, preferably 20 to about 330 Oe; the saturation magnetization value in a magnetic field of 10 kOe is usually about 50 to about 91 emu/g, preferably about 60 to about 90 emu/g; and the residual magnetization value in a magnetic field of 10 kOe is usually about 1 to about 35 emu/g, preferably about 3 to about 30 emu/g.

[0045] The particle shape and particle size of the black magnetic composite particles according to the present invention are considerably varied depending upon those of the magnetic iron oxide particles as core particles. The black magnetic composite particles have a similar particle shape to that of the magnetic iron oxide particle as core particle, and a slightly larger particle size than that of the magnetic iron oxide particles as core particles.

[0046] More specifically, when the isotropic magnetic iron oxide particles are used as core particles, the obtained black magnetic composite particles according to the present invention, have an average particle size of usually 0.06 to 1.0 μm, preferably 0.07 to 0.8 μm, more preferably 0.07 to 0.5 μm and a ratio of an average particle length to an average particle breadth of usually not less than 1.0 and less than 2.0, preferably 1.0 to 1.8, more preferably 1.0 to 1.5,. When the anisotropic magnetic iron oxide particles are used as core particles, the obtained black magnetic composite particles according to the present invention, have an average particle size of usually 0.06 to 1.0 μm, preferably 0.07 to 0.8 μm, more preferably 0.07 to 0.5 μm.

[0047] When the average particle size of the black magnetic composite particles is more than 1.0 μm, the obtained black magnetic composite particles may be coarse particles, and deteriorated in tinting strength. On the other hand, when the average particle size thereof is less than 0.06 μm, the black magnetic composite particles tends to be agglomerated by the increase of intermolecular force due to the reduction in particle size, thereby deteriorating the dispersibility in a binder resin upon production of the magnetic toner.

[0048] When the anisotropic magnetic iron oxide particles are used as core particles, the upper limit of the aspect ratio of the obtained black magnetic composite particles according to the present invention, is usually 20:1, preferably 18:1, more preferably 15:1. When the aspect ratio is more than 20:1, the black magnetic composite particles may be entangled with each other in the binder resin, so that the dispersibility in binder resin tends to be deteriorated.

[0049] The geometrical standard deviation value of the black magnetic composite particles according to the present invention is preferably not more than 2.0, more preferably 1.01 to 1.8, still more preferably 1.01 to 1.6. The lower limit of the geometrical standard deviation value thereof is preferably 1.01. When the geometrical standard deviation value thereof is more than 2.0, the tinting strength of the black magnetic composite particles is likely to be deteriorated due to the existence of coarse particles therein. It is industrially difficult to obtain such particles having a geometrical standard deviation of less than 1.01.

[0050] The BET specific surface area of the black magnetic composite particles according to the present invention, is usually 1 to 200 m^2/g, preferably 2 to 150 m^2/g, more preferably 2.5 to 100 m^2/g. When the BET specific surface area thereof is less than 1 m^2/g, the obtained black magnetic composite particles may be coarse, and the sintering between the black magnetic composite particles is caused, thereby deteriorating the tinting strength. On the other hand, when the BET specific surface area is more than 200 m^2/g, the black magnetic composite particles tend to be agglomerated together by the increase in intermolecular force due to the reduction in particle size, thereby deteriorating th dispersibility in a bind r resin upon production of the magnetic toner.

[0051] As to th fluidity of th black magnetic composite particles according to the present invention, the fluidity index thereof is preferably 45 to 80, mor preferably 46 to 80, still more pr ferably 47 to 80. When the fluidity index ther of is less than 45, the fluidity of the black magnetic composite particles becomes insufficient, th reby failing to improve the fluidity of th finally obtained magn tic toner. Further, in the production proc ss of the magn tic ton r, th re tend to be caus d defects such as clogging of hopper, etc., th reby d t riorating the handling property or workability.

[0052] As to the blackness of the black magnetic composite particles according to the present inv ntion, in the case magnetite particles are used as core particles, the upper limit of th blackn ss of the black magnetic composite particles is usually 20.0, preferably 19.0, more preferably 18.0 when r pres nted by L* value. In th case maghemite particles are used as core particles, the upper limit of the blackness of the black magnetic composite particles is usually 20.0, preferably 19.5, more preferably 19.0 when represented by L* value. When the L* value thereof is more than 20.0, the lightness of the obtained black magnetic composite particles becomes high, so that the black magnetic composite particles having a sufficient blackness cannot be obtained. The lower limit of the blackness thereof is 15 when represented by L* value.

[0053] The dispersibility in binder resin of the black magnetic composite particles according to the present invention, is preferably 4th or 5th rank, more preferably 5th rank when evaluated by the method described hereinafter.

[0054] The percentage of desorption of carbon black fine particles from the black magnetic composite particles according to the present invention, is preferably not more than 20 %, more preferably not more than 10 %. When the desorption percentage of the carbon black fine particles is more than 20 %, the desorbed carbon black fine particles tend to inhibit the black magnetic composite particles from being uniformly dispersed in the binder resin upon production of the magnetic toner.

[0055] The magnetic properties of the black magnetic composite particles according to the present invention, can be controlled by appropriately selecting kind and particle shape of the magnetic iron oxide particles as core particles. Similarly to magnetic properties of magnetic particles ordinarily used for the production of magnetic toner, the coercive force of the black magnetic composite particles according to the present invention, is usually about 10 to about 350 Oe, preferably about 20 to about 330 Oe; the saturation magnetization in a magnetic field of 10 kOe is usually about 50 to about 91 emu/g, preferably about 60 to about 90 emu/g; and the residual magnetization in a magnetic field of 10 kOe is usually about 1 to about 35 emu/g, preferably about 3 to about 30 emu/g.

[0056] The coating formed on the surfaces of the core particles comprises at least one organosilicon compound selected from the group consisting of (1) organosilane compounds obtained by drying or heat-treating alkoxysilane compounds; (2) polysiloxanes, or modified polysiloxanes selected from the group consisting of (A) polysiloxanes modified with at least one compound selected from the group consisting of polyethers, polyesters and epoxy compounds (hereinafter referred to merely as "modified polysiloxanes"), and (B) polysiloxanes whose molecular terminal is modified with at least one group selected from the group consisting of carboxylic acid groups, alcohol groups and a hydroxyl group; and (3) fluoroalkyl organosilane compounds obtained by drying or heat-treating fluoroalkylsilane compounds.

[0057] The organosilane compounds (1) can be produced by drying or heat-treating alkoxysilane compounds represented by the formula (I):

$$R^1{}_aSiX_{4-a} \qquad (I)$$

wherein R^1 is C_6H_5-, $(CH_3)_2CHCH_2$- or n-C_bH_{2b+1}- (wherein b is an integer of 1 to 18); X is CH_3O- or C_2H_5O-; and a is an integer of 0 to 3.

[0058] The drying or heat-treatment of the alkoxysilane compounds is conducted, for example, at a temperature of usually 40 to 200°C, preferably 60 to 150°C for usually 10 minutes to 12 hours, preferably 30 minutes to 3 hours.

[0059] Specific examples of the alkoxysilane compounds may include methyl triethoxysilane, dimethyl diethoxysilane, tetraethoxysilane, phenyl triethyoxysilane, diphenyl diethoxysilane, methyl trimethoxysilane, dimethyl dimethoxysilane, tetramethoxysilane, phenyl trimethoxysilane, diphenyl dimethoxysilane, isobutyl trimethoxysilane, decyl trimethoxysilane or the like. Among these alkoxysilane compounds, in view of the desorption percentage and the adhering effect of carbon black fine particles, methyl triethoxysilane, phenyl triethyoxysilane, methyl trimethoxysilane, dimethyl dimethoxysilane and isobutyl trimethoxysilane are preferred, and methyl triethoxysilane and methyl trimethoxysilane are more preferred.

[0060] As the polysiloxanes (2), there may be used those compounds represented by the formula (II):

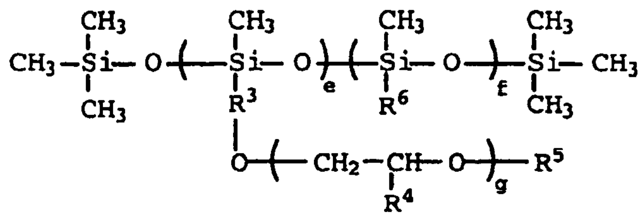
$$CH_3-\underset{CH_3}{\overset{CH_3}{Si}}-O\left(\underset{CH_3}{\overset{R^2}{Si}}-O\right)_d\underset{CH_3}{\overset{CH_3}{Si}}-CH_3 \qquad (II)$$

wherein R^2 is H- or CH_3-, and d is an int g r of 15 to 450.

[0061] Among thes polysiloxanes, in view of the desorption percentage and the adhering effect of carbon black fine particles, polysiloxanes having methyl hydrogen siloxane units ar pr ferr d.

[0062] As th modified polysiloxanes (A), there may be used:

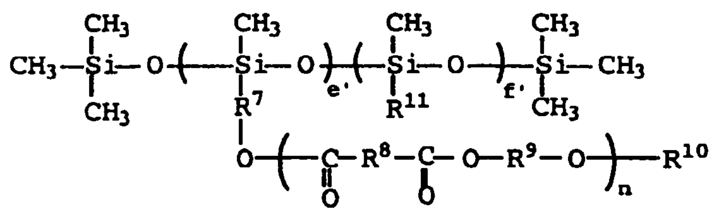
(a) polysiloxanes modified with polyethers represented by the formula (III):



(III)

wherein R^3 is $-(-CH_2-)_h-$; R^4 is $-(-CH_2-)_i-CH_3$; R^5 is -OH, -COOH, $-CH=CH_2$, $-C(CH_3)=CH_2$ or $-(-CH_2-)_j-CH_3$; R^6 is $-(-CH_2-)_k-CH_3$; g and h are an integer of 1 to 15; i, j and k are an integer of 0 to 15; e is an integer of 1 to 50; and f is an integer of 1 to 300;

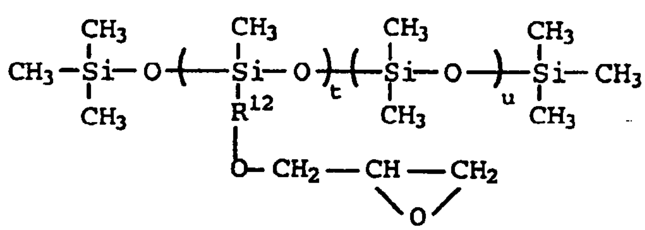
(b) polysiloxanes modified with polyesters represented by the formula (IV):



(IV)

wherein R^7, R^8 and R^9 are $-(-CH_2-)_q-$ and may be the same or different; R^{10} is -OH, -COOH, $-CH=CH_2$, $-C(CH_3)=CH_2$ or $-(-CH_2-)_r-CH_3$; R^{11} is $-(-CH_2-)_s-CH_3$; n and q are an integer of 1 to 15; r and s are an integer of 0 to 15; e' is an integer of 1 to 50; and f' is an integer of 1 to 300;

(c) polysiloxanes modified with epoxy compounds represented by the formula (V):



(V)

wherein R^{12} is $-(-CH_2-)_v-$; v is an integer of 1 to 15; t is an integer of 1 to 50; and u is an integer of 1 to 300; or a mixture thereof.

[0063] Among these modified polysiloxanes (A), in view of the desorption percentage and the adhering effect of carbon black fin particles, th polysiloxanes modified with the polyether repr s nt d by the formula (III), ar preferred.

[0064] As the t rminal-modifi d polysiloxanes (B), there may be used those represented by the formula (VI):

$$R^{13}-\underset{CH_3}{\overset{CH_3}{Si}}-O-\left(\underset{CH_3}{\overset{CH_3}{Si}}-O\right)_w\left(\underset{CH_3}{\overset{R^{15}}{Si}}-O\right)_x\underset{CH_3}{\overset{CH_3}{Si}}-R^{14} \qquad (VI)$$

wherein R^{13} and R^{14} are -OH, $R^{16}OH$ or $R^{17}COOH$ and may be the same or different; R^{15} is $-CH_3$ or $-C_6H_5$; R^{16} and R^{17} are $-(-CH_2-)_y-$; y is an integer of 1 to 15; w is an integer of 1 to 200; and x is an integer of 0 to 100.

[0065] Among these terminal-modified polysiloxanes, in view of the desorption percentage and the adhering effect of carbon black fine particles, the polysiloxanes whose terminals are modified with carboxylic acid groups are preferred.

[0066] The fluoroalkyl organosilane compounds (3) may be produced by drying or heat-treating fluoroalkylsilane compounds represented by the formula (VII):

$$CF_3(CF_2)_zCH_2CH_2(R^{18})_{a'}SiX_{4-a'} \qquad (VII)$$

wherein R^{18} is CH_3-, C_2H_5-, CH_3O- or C_2H_5O-; X is CH_3O- or C_2H_5O-; and z is an integer of 0 to 15; and a' is an integer of 0 to 3.

[0067] The drying or the heat-treatment of the fluoroalkylsilane compounds may be conducted, for example, at a temperature of usually 40 to 200°C, preferably 60 to 150°C for usually 10 minutes to 12 hours, preferably 30 minutes to 3 hours.

[0068] Specific examples of the fluoroalkylsilane compounds may include trifluoropropyl trimethoxysilane, tridecafluorooctyl trimethoxysilane, heptadecafluorodecyl trimethoxysilane, heptadecafluorodecylmethyl dimethoxysilane, trifluoropropyl triethoxysilane, tridecafluorooctyl triethoxysilane, heptadecafluorodecyl triethoxysilane, heptadecafluorodecylmethyl diethoxysilane or the like. Among these fluoroalkylsilane compounds, in view of the desorption percentage and the adhering effect of carbon black fine particles, trifluoropropyl trimethoxysilane, tridecafluorooctyl trimethoxysilane and heptadecafluorodecyl trimethoxysilane are preferred, and trifluoropropyl trimethoxysilane and tridecafluorooctyl trimethoxysilane are more preferred.

[0069] The coating amount of the organosilicon compounds is usually 0.02 to 5.0 % by weight, preferably 0.03 to 2.0 % by weight, more preferably 0.05 to 1.5 % by weight (calculated as Si) based on the weight of the acicular hematite particles or the acicular iron oxide hydroxide particles coated with the organosilicon compounds.

[0070] When the coating amount of the organosilicon compounds is less than 0.02 % by weight, it becomes difficult to adhere the carbon black fine particles on the surfaces of the magnetic iron oxide particles in such an amount enough to improve the fluidity and blackness of the obtained black magnetic composite particles.

[0071] On the other hand, when the coating amount of the organosilicon compounds is more than 5.0 % by weight, a sufficient amount of the carbon black fine particles can be adhered on the surfaces of the magnetic iron oxide particles. However, the use of such unnecessarily large amount of the organosilicon compounds is meaningless because the effect of enhancing the fluidity or blackness of the obtained black magnetic composite particles is already saturated.

[0072] As the carbon black fine particles used in the black magnetic composite particles according to the present invention, there may be exemplified commercially available carbon black particles such as furnace black, channel black or the like. Specific examples of the commercially available carbon black particles usable in the present invention, may include MA100, MA7, #1000, #2400B, #30, MA8, MA11, #50, #52, #45, #2200B, MA600, etc. (tradenames; produced by Mitsubishi Chemical Corp.), Seast9H, Seast7H, Seast6, Seast3H, Seast300, SeastFM, etc. (tradenames; produced by Tokai Carbon Co., Ltd.) or the like. In the consideration of compatibility with the organosilicon compounds, MA100, MA7, #1000, #2400B and #30 are preferred.

[0073] The average particle size of the carbon black fine particles is usually about 0.002 to about 0.05 μm, preferably about 0.002 to about 0.035 μm.

[0074] When the average particle size of the carbon black fine particles is less than 0.002 μm, the carbon black fine particles are too fine to be well handled.

[0075] On the other hand, when the average particle size of the carbon black fine particles is more than 0.05 μm, th particle size of th carbon black fine particl s becom s much larger than that of the magnetic iron oxide particles as core particles, ther by causing insufficient adh sion of the carbon black fine particl s onto the coating composed of the organosilicon compounds, and increasing the desorption percentage of the carbon black fine particles. As a result, the obtained black magnetic composite particles tend to be deteriorat d in dispersibility in a binder resin upon the production of magnetic toner.

[0076] The ratio of th average particle size of the magnetic iron oxide particles to that of the carbon black fine particles is preferably not less than 2:1. When th ratio is less than 2:1, the particle size of th carbon black fine particles becomes considerably larger as compared to that of the magnetic iron oxid particles as core particles, thereby causing insufficient adhesion of the carbon black fine particles onto the coating composed of the organosilicon compounds, and increasing the desorption percentage of the carbon black fine particles. As a result, the obtained black magnetic composite particles tend to be deteriorated in dispersibility in a binder resin upon the production of magnetic toner.

[0077] The amount of the carbon black fine particles adhered is 1 to 25 parts by weight based on 100 parts by weight of the magnetic iron oxide particles as core particles.

[0078] When the amount of the carbon black fine particles adhered is less than 1 part by weight, the amount of the carbon black fine particles adhered is insufficient, so that it becomes difficult to obtain black magnetic composite particles having a sufficient fluidity and blackness .

[0079] On the other hand, when the amount of the carbon black fine particles adhered is more than 25 parts by weight, the obtained black magnetic composite particles can show a sufficient fluidity and blackness. However, since the amount of the carbon black fine particles adhered is considerably large, the carbon black fine particles tend to be desorbed from the coating composed of the organosilicon compound. As a result, the obtained black magnetic composite particles tend to be deteriorated in dispersibility in a binder resin upon the production of magnetic toner.

[0080] In the black magnetic composite particles according to the present invention, the surfaces of the magnetic iron oxide particles as core particles may be preliminarily coated with at least one compound selected from the group consisting of hydroxides of aluminum, oxides of aluminum, hydroxides of silicon and oxides of silicon (hereinafter referred to as "coating composed of hydroxides and/or oxides of aluminum and/or silicon"), if necessary. In this case, the obtained black magnetic composite particles can show a higher dispersibility in a binder resin as compared to in the case where the magnetic iron oxide particles are uncoated with hydroxides and/or oxides of aluminum and/or silicon.

[0081] The coating amount of the hydroxides and/or oxides of aluminum and/or silicon is preferably 0.01 to 50 % by weight (calculated as Al, SiO_2 or a sum of Al and SiO_2) based on the weight of the magnetic iron oxide particles as core particles.

[0082] When the coating amount of the hydroxides and/or oxides of aluminum and/or silicon is less than 0.01 % by weight, the effect of enhancing the dispersibility of the obtained black magnetic composite particles in a binder resin upon the production of magnetic toner cannot be obtained.

[0083] On the other hand, when the coating amount of the hydroxides and/or oxides of aluminum and/or silicon is more than 50 % by weight, the obtained black magnetic composite particles can exhibit a good dispersibility in a binder resin upon the production of magnetic toner. However, the use of such unnecessarily large coating amount of the hydroxides and/or oxides of aluminum and/or silicon is meaningless.

[0084] The particle size, geometrical standard deviation, BET specific surface area, fluidity, blackness L* value and desorption percentage of carbon black fine particles of the black magnetic composite particles wherein the surface of the core particle is coated with the hydroxides and/or oxides of aluminum and/or silicon according to the present invention, are substantially the same as those of the black magnetic composite particles wherein the core particle is uncoated with the hydroxides and/or oxides of aluminum and/or silicon according to the present invention.

[0085] The black magnetic composite particles according to the present invention can be produced by the following method.

[0086] Among the isotropic magnetite particles which are magnetic iron oxide particles, (1) octahedral magnetite particles can be produced by passing an oxygen-containing gas through a suspension containing ferrous hydroxide colloid having a pH value of not less than 10, which is obtained by reacting an aqueous ferrous salt solution with an aqueous alkali solution having a concentration of not less than one equivalent based on Fe^{2+} in the aqueous ferrous salt solution, thereby precipitating magnetite particles, and then subjecting the obtained magnetite particles to filtering, washing with water and drying (Japanese Patent Publication (KOKOKU) No. 44-668(1969); (2) hexahedral magnetite particles can be produced by passing an oxygen-containing gas through a suspension containing ferrous hydroxide colloid having a pH value of 6.0 to 7.5, which is obtained by reacting an aqueous ferrous salt solution with an aqueous alkali solution having a concentration of not more than one equivalent based on Fe^{2+} in the aqueous ferrous salt solution to produce magnetite core particles, further passing an oxygen-containing gas through the obtained aqueous ferrous salt reaction solution containing the magnetite core particles and the ferrous hydroxide colloid, at a pH value of 8.0 to 9.5, to precipitate magnetite particles, and then subjecting the precipitated magnetite particles to filtering, washing with water and drying (Japanese Patent Application Laid-Open (KOKAI) No. 3-201509(1991); (3) spherical magnetite particles can be produced by passing an oxygen-containing gas through a suspension containing ferrous hydroxide colloid having a pH value of 6.0 to 7.5, which is obtained by reacting an aqu ous ferrous salt solution with an aqueous alkali solution having a conc ntration of not more than on equival nt bas d on Fe^{2+} in the aqueous ferrous salt solution to produce magn tite core particles, adding alkali hydroxide in an amount of not less than equivalent based on the remaining Fe^{2+} to adjust the pH value of th suspension to not less than 10, heat-oxidizing the resultant suspension to precipitate magnetite particles, and then subjecting the precipitated magnetit particles to filtering, washing with water

and drying (Japanese Patent Publication (KOKOKU) No. 62-51208(1987).

[0087] The isotropic maghemite particl s can be obtained by heating the above-mention d isotropic magn tite particles in air at 300 to 600°C.

[0088] The anisotropic magnetite particles can be produced by passing an oxygen-containing gas through a suspension containing either ferrous hydroxide colloid, iron carbonate, or an iron-containing precipitate obtained by reacting an aqueous ferrous salt solution with alkali hydroxide and/or alkali carbonate, while appropriately controlling the pH value and temperature of the suspension, to produce acicular, spindle-shaped or rice ball-shaped goethite particles, subjecting the obtained goethite particles to filtering, washing with water and drying, and then reducing the goethite particles in a heat-reducing gas at 300 to 800°C.

[0089] The anisotropic maghemite particles can be produced by heat-oxidizing the above-mentioned anisotropic magnetite particles in an oxygen-containing gas at 300 to 600°C.

[0090] The coating of the magnetic iron oxide particles with the alkoxysilane compounds, the polysiloxanes, the modified polysiloxanes, the terminal-modified polysiloxanes or the fluoroalkylsilane compounds, may be conducted by mechanically mixing and stirring the magnetic iron oxide particles together with the alkoxysilane compounds, the polysiloxanes, the modified polysiloxanes, the terminal-modified polysiloxanes or the fluoroalkylsilane compounds; or by mechanically mixing and stirring both the components together while spraying the alkoxysilane compounds, the polysiloxanes, the modified polysiloxanes, the terminal-modified polysiloxanes or the fluoroalkylsilane compounds onto the magnetic iron oxide particles. In these cases, substantially whole amount of the alkoxysilane compounds, the polysiloxanes, the modified polysiloxanes, the terminal-modified polysiloxanes or the fluoroalkylsilane compounds added can be applied onto the surfaces of the magnetic iron oxide particles.

[0091] In order to uniformly coat the surfaces of the magnetic iron oxide particles with the alkoxysilane compounds, the polysiloxanes, the modified polysiloxanes, the terminal-modified polysiloxanes or the fluoroalkylsilane compounds, it is preferred that the magnetic iron oxide particles are preliminarily diaggregated by using a pulverizer. As the apparatuses for the mixing and stirring, there may be used an edge runner, a Henschel mixer or the like.

[0092] The conditions for the mixing and stirring such as mixing ratio, linear load, stirring speed or mixing and stirring time, may be appropriately adjusted so as to coat the surfaces of the magnetic iron oxide particles with the alkoxysilane compounds, the polysiloxanes, the modified polysiloxanes, the terminal-modified polysiloxanes or the fluoroalkylsilane compounds as uniformly as possible. The mixing and stirring time for the coating treatment is, for example, preferably not less than 20 minutes.

[0093] The amount of the alkoxysilane compounds, the polysiloxanes, the modified polysiloxanes, the terminal-modified polysiloxanes or the fluoroalkylsilane compounds added, is preferably 0.15 to 45 parts by weight based on 100 parts by weight of the magnetic iron oxide particles. When the amount of the organosilicon compounds added is less than 0.15 part by weight, it may become difficult to adhere the carbon black fine particles in such an amount enough to improve the blackness and flowability of the obtained black magnetic composite particles. On the other hand, when the amount of the organosilicon compounds added is more than 45 parts by weight, a sufficient amount of the carbon black fine particles can be adhered on the surface of the coating, but it is meaningless because the blackness and volume resistivity of the composite particles cannot be further improved by using such an excess amount of the organosilicon compounds.

[0094] Next, the carbon black fine particles are added to the magnetic iron oxide particles coated with the organosilicon compounds, and the resultant mixture is mixed and stirred to adhere the carbon black fine particles on the surfaces of the coating composed of the organosilicon compounds, and then dried.

[0095] In the case where the alkoxysilane compounds (1) and the fluoroalkylsilane compounds (3) are used as the coating compound, after the carbon black fine particles are adhered on the surface of the coating, the resultant composite particles are dried or heat-treated, for example, at a temperature of usually 40 to 200°C, preferably 60 to 150°C for usually 10 minutes to 12 hours, preferably 30 minutes to 3 hours, thereby forming a coating composed of the organosilane compounds (1) and the fluoroalkyl organosilane compounds (3), respectively.

[0096] It is preferred that the carbon black fine particles are added little by little and slowly, especially about 5 to 60 minutes.

[0097] The conditions for mixing and stirring the magnetic iron oxide particles and the carbon black fine particles coated with the organosilicon compounds, such as mixing ratio, linear load stirring speed or mixing and stirring time, may be appropriately adjusted so as to uniformly adhere the carbon black fine particles on the surface of the coating. The mixing and stirring time for the adhesion treatment is, for example, preferably not less than 20 minutes.

[0098] The amount of the carbon black fin particl s added, is preferably 1 to 30 parts by weight bas d on 100 parts by weight of th magnetic iron oxide particles. When the amount of the carbon black fine particles added is less than 1 part by weight, it may become difficult to adhere the carbon black fine particles in such an amount enough to improve the blackness and flowability of the obtained composite particles. On the other hand, wh n the amount of the carbon black fine particles added is more than 30 parts by weight, a sufficient blackness and flowability of the r sultant composit particles can be obtained, but the carbon black fine particles tend to be desorb d from th surfac of the coating

becaus of too large amount of the carbon black fine particles adhered, resulting in deteriorat d dispersibility in the binder resin upon the production of th magnetic toner.

[0099] The magnetic iron oxide particles may be coated with at least on compound selected from th group consisting of hydroxides of aluminum, oxides of aluminum, hydroxides of silicon and oxides of silicon, if requir d, prior to mixing and stirring with the alkoxysilane compounds, the polysiloxanes, the modified polysiloxanes, the terminal-modified polysiloxanes or the fluoroalkylsilane compounds.

[0100] The coating of the hydroxides and/or oxides of aluminum and/or silicon may be conducted by adding an aluminum compound, a silicon compound or both the compounds to a water suspension in which the magnetic iron oxide particles are dispersed, followed by mixing and stirring, and further adjusting the pH value of the suspension, if required, thereby coating the surfaces of the magnetic iron oxide particles with at least one compound selected from the group consisting of hydroxides of aluminum, oxides of aluminum, hydroxides of silicon and oxides of silicon. The thus obtained particles coated with the hydroxides and/or oxides of aluminum and/or silicon are then filtered out, washed with water, dried and pulverized. Further, the particles coated with the hydroxides and/or oxides of aluminum and/or silicon may be subjected to posttreatments such as deaeration treatment and compaction treatment, if required.

[0101] As the aluminum compounds, there may be exemplified aluminum salts such as aluminum acetate, aluminum sulfate, aluminum chloride or aluminum nitrate, alkali aluminates such as sodium aluminate, alumina sols or the like.

[0102] The amount of the aluminum compound added is 0.01 to 50 % by weight (calculated as Al) based on the weight of the magnetic iron oxide particles. When the amount of the aluminum compound added is less than 0.01 % by weight, it may be difficult to sufficiently coat the surfaces of the magnetic iron oxide particles with hydroxides and/or oxides of aluminum, thereby failing to achieve the improvement of the dispersibility in the binder resin upon the production of the magnetic toner. On the other hand, when the amount of the aluminum compound added is more than 50 % by weight, the coating effect is saturated and, therefore, it is meaningless to add such an excess amount of the aluminum compound.

[0103] As the silicon compounds, there may be exemplified #3 water glass, sodium orthosilicate, sodium metasilicate, colloidal silica or the like.

[0104] The amount of the silicon compound added is 0.01 to 50 % by weight (calculated as SiO_2) based on the weight of the magnetic iron oxide particles. When the amount of the silicon compound added is less than 0.01 % by weight, it may be difficult to sufficiently coat the surfaces of the magnetic iron oxide particles with hydroxides and/or oxides of silicon, thereby failing to achieve the improvement of the dispersibility in the binder resin upon the production of the magnetic toner. On the other hand, when the amount of the silicon compound added is more than 50 % by weight, the coating effect is saturated and, therefore, it is meaningless to add such an excess amount of the silicon compound.

[0105] In the case where both the aluminum and silicon compounds are used in combination for the coating, the total amount of the aluminum and silicon compounds added is preferably 0.01 to 50 % by weight (calculated as a sum of Al and SiO_2) based on the weight of the magnetic iron oxide particles.

[0106] Next, the black magnetic toner according to the present invention is described.

[0107] The black magnetic toner according to the present invention comprises the black magnetic composite particles, and a binder resin. The black magnetic toner may further contain a mold release agent, a colorant, a charge-controlling agent and other additives, if necessary.

[0108] The black magnetic toner according to the present invention has an average particle size of usually 3 to 15 µm, preferably 5 to 12 µm.

[0109] The amount of the binder resin used in the black magnetic toner is usually 50 to 900 parts by weight, preferably 50 to 400 parts by weight based on 100 parts by weight of the black magnetic composite particles.

[0110] As the binder resins, there may be used vinyl-based polymers, i.e., homopolymers or copolymers of vinyl-based monomers such as styrene, alkyl acrylates and alkyl methacrylates. As the styrene monomers, there may be exemplified styrene and substituted styrenes. As the alkyl acrylate monomers, there may be exemplified acrylic acid, methyl acrylate, ethyl acrylate, butyl acrylate or the like.

[0111] It is preferred that the above copolymers contain styrene-based components in an amount of usually 50 to 95 % by weight.

[0112] In the binder resin used in the present invention, the above-mentioned vinyl-based polymers may be used in combination with polyester-based resins, epoxy-based resins, polyurethane-based resins or the like, if necessary.

[0113] As to the fluidity of the black magnetic toner according to the present invention, the fluidity index is usually 70 to 100, preferably 71 to 100, more preferably 72 to 100. When the fluidity index is less than 70, the black magnetic toner may not show a sufficient fluidity.

[0114] The blackness of the black magnetic toner according to the present invention is usually not more than 20, preferably not more than 19.8, more preferably not more than 19.5 when r presented by L* valu . Wh n the blackn ss thereof is more than 20, the lightness of the black magnetic t ner may be increased, r sulting in insufficient blackness. The lower limit of the blackness of the black magnetic ton r is usually about 15 when r pr sented by L* valu .

[0115] The volume r sistivity of the black magn tic ton r according to the present invention, is usually not less than

1.0×10^{13} Ω•cm, pref rably not less than 3.0×10^{13} Ω•cm, more preferably not less than 5.0×10^{13} Ω•cm. When the volume resistivity is less than 1.0×10^{13} Ω•cm, the charge amount of th black magnetic toner tends to vary dep nding upon environm ntal conditions in which the toner is used, resulting in unstabl properties of the black magn tic toner. The upper limit of th volume resistivity is 1.0×10^{17} Ω•cm.

[0116] As to the magnetic properties of the black magnetic toner according to the present invention, the coercive force thereof is usually 10 to 350 Oe, preferably 20 to 330 Oe; the saturation magnetization value in a magnetic field of 10 kOe is usually 10 to 85 emu/g, preferably 20 to 80 emu/g; the residual magnetization in a magnetic field of 10 kOe is usually 1 to 20 emu/g, preferably 2 to 15 emu/g; the saturation magnetization in a magnetic field of 1 kOe is usually 7.5 to 65 emu/g, preferably 10 to 60 emu/g; and the residual magnetization in a magnetic field of 1 kOe is usually 0.5 to 15 emu/g, preferably 1.0 to 13 emu/g.

[0117] The black magnetic toner according to the present invention may be produced by a known method of mixing and kneading a predetermined amount of a binder resin and a predetermined amount of the black magnetic composite particles together, and then pulverizing the mixed and kneaded material into particles. More specifically, the black magnetic composite particles and the binder resin are intimately mixed together with, if necessary, a mold release agent, a colorant, a charge-controlling agent or other additives by using a mixer. The obtained mixture is then melted and kneaded by a heating kneader so as to render the respective components compatible with each other, thereby dispersing the black magnetic composite particles therein. Successively, the molten mixture is cooled and solidified to obtain a resin mixture. The obtained resin mixture is then pulverized and classified, thereby producing a magnetic toner having an aimed particle size.

[0118] As the mixers, there may be used a Henschel mixer, a ball mill or the like. As the heating kneaders, there may be used a roll mill, a kneader, a twin-screw extruder or the like. The pulverization of the resin mixture may be conducted by using pulverizers such as a cutter mill, a jet mill or the like. The classification of the pulverized particles may be conducted by known methods such as air classification, etc., as described in Japanese Patent No. 2683142 or the like.

[0119] As the other method of producing the black magnetic toner, there may be exemplified a suspension polymerization method or an emulsion polymerization method. In the suspension polymerization method, polymerizable monomers and the black magnetic composite particles are intimately mixed together with, if necessary, a colorant, a polymerization initiator, a cross-linking agent, a charge-controlling agent or the other additives and then the obtained mixture is dissolved and dispersed together so as to obtain a monomer composition. The obtained monomer composition is added to a water phase containing a suspension stabilizer while stirring, thereby granulating and polymerizing the composition to form magnetic toner particles having an aimed particle size.

[0120] In the emulsion polymerization method, the monomers and the black magnetic composite particles are dispersed in water together with, if necessary, a colorant, a polymerization initiator or the like and then the obtained dispersion is polymerized while adding an emulsifier thereto, thereby producing magnetic toner particles having an aimed particle size.

[0121] An important point of the present invention exists in that the black magnetic composite particles comprising the magnetic iron oxide particles which have an average particle size of 0.055 to 0.95 µm and may be coated with at least one compound selected from the group consisting of hydroxides of aluminum, oxides of aluminum, hydroxides of silicon and oxides of silicon; the organosilicon compounds coated on at least a part of the surface of the magnetic iron oxide particle; the carbon black fine particles having an average particle size of 0.002 to 0.05 µm, which are adhered on the surface of the coating composed of the organosilicon compounds, in which the total amount of the carbon black fine particles adhered to the coating composed of the organosilicon compounds is 1 to 25 parts by weight based on 100 parts by weight of the magnetic iron oxide particles, can show not only excellent fluidity and blackness, but also an excellent dispersibility in a binder resin upon the production of magnetic toner due to less amount of carbon black fine particles desorbed or fallen-off from the surfaces of the particles.

[0122] The reason why the amount of the carbon black fine particles desorbed or fallen-off from the surfaces of the black magnetic composite particles according to the present invention, is small, is considered as follows. That is, the surfaces of the magnetic iron oxide particles and the organosilicon compounds are strongly bonded to each other, so that the carbon black fine particles bonded to the surfaces of the magnetic iron oxide particles through the organosilicon compounds can be prevented from being desorbed from the magnetic iron oxide particles.

[0123] In particular, in the case of the alkoxysilane compounds (1) and the fluoroalkylsilane compounds (3), metalosiloxane bonds (≡Si-O-M wherein M represents a metal atom contained in the black iron oxide particles, such as Si, Al, Fe or the like) are formed between the surfaces of th magnetic iron oxide particles and alkoxy groups contained in the organosilicon compounds onto which the carbon black fine particles are adhered, thereby forming a stronger bond b tw en th organosilicon compounds on which the carbon black fine particles are adhered, and the surfaces of th magnetic iron oxid particles.

[0124] The reason why th black magnetic composite particles according to the pr sent invention can show an xcellent disp rsibility in a binder resin upon the production of magnetic ton r, is considered such that since only a

small amount of the carbon black fine particles are desorbed or fallen-off from the surfaces of the black magnetic composite particles, the black magnetic composite particles is fre from deterioration in dispersibility due to th desorbed or fallen-off carbon black fine particles, and further since the carbon black fine particles are adh red onto the surfaces of the black magnetic composite particles and, therefore, irregularities are formed on the surfaces of the black magnetic composite particles, the contact between the particles can be suppressed.

[0125] The reason why the black magnetic composite particles according to the present invention can show an excellent fluidity, is considered as follows. That is, the carbon black fine particles which are ordinarily agglomerated together due to fineness thereof, are allowed to be uniformly and densely adhered on the surfaces of the magnetic iron oxide particles and, therefore, can be dispersed nearly in the form of primary particles, so that many fine irregularities are formed on the surfaces of the magnetic iron oxide particles.

[0126] The reason why the black magnetic composite particles according to the present invention can show an excellent blackness, is considered such that since the carbon black fine particles are uniformly and densely adhered on the surfaces of the magnetic iron oxide particles, the color tone of the core particles is hidden behind the carbon black fine particles, so that an inherent color tone of carbon black can be exhibited.

[0127] Therefore, the black magnetic toner produced by using the above black magnetic composite particles, can show excellent fluidity and blackness.

[0128] The reason why the black magnetic toner according to the present invention can show an excellent fluidity, is considered as follows. That is, the black magnetic composite particles on which a large amount of the carbon black fine particles are uniformly adhered, are blended in the black magnetic toner, so that many fine irregularities are formed on the surface of the black magnetic toner.

[0129] The reason why the black magnetic toner according to the present invention can show an excellent blackness, is considered such that the black magnetic composite particles having an excellent blackness is blended in the black magnetic toner.

[0130] As described above, since the black magnetic composite particles according to the present invention, are excellent not only in fluidity and blackness, but also in dispersibility in a binder resin due to less amount of the carbon black fine particles desorbed or fallen-off from the surfaces thereof, the black magnetic composite particles according to the present invention, are suitable as black magnetic particles for black magnetic toner capable of attaining a high image quality and a high copying speed.

[0131] In addition, since the black magnetic composite particles according to the present invention, are excellent in dispersibility in a binder resin, the particles can show excellent handling property and workability and, therefore, are preferable from an industrial viewpoint.

[0132] Further, the black magnetic toner produced from the above black magnetic composite particles which are excellent in fluidity and blackness, can also show excellent fluidity and blackness. Accordingly, the black magnetic toner is suitable as black magnetic toner capable of attaining a high image quality and a high copying speed.

[0133] Furthermore, in the black magnetic toner according to the present invention, since the black magnetic composite particles contained therein are excellent in dispersibility, it is possible to expose the black magnetic composite particles to the surface of the black magnetic toner independently and separately. As a result, the black magnetic toner can be free from being deteriorated in electric resistance due to the existence of the carbon black fine particles. Accordingly, the black magnetic toner according to the present invention is suitable as a high-resistance or insulated magnetic toner.

EXAMPLES

[0134] The present invention is described in more detail by Examples and Comparative Examples, but the Examples are only illustrative and, therefore, not intended to limit the scope of the present invention.

[0135] Various properties were measured by the following methods.

(1) The average particle size, the average major axial diameter and average minor axial diameter of magnetite particles, maghemite particles, black magnetic composite particles and carbon black fine particles were respectively expressed by the average of values (measured in a predetermined direction) of about 350 particles which were sampled from a micrograph obtained by magnifying an original electron micrograph (X 20,000) by four times in each of the longitudinal and transverse directions.

(2) The asp ct ratio of the particles was expr ssed by the ratio of averag major axial diameter to av rag minor axial diameter thereof.

(3) The geometrical standard d viation of particle sizes was expressed by values obtained by the following method. That is, the particle sizes (major axial diamet rs) were measured from the above magnified electron micrograph. The actual particle sizes (major axial diameters) and th number of the particles w re calculated from th measured values. On a logarithmic normal probability pap r, the particle sizes (major axial diameters) wer plotted at regular

intervals on the abscissa-axis and the accumulative number (under integration si v) of particles belonging to each interval of the particle siz s (major axial diamet rs) w re plotted by percentage on the ordinate-axis by a statistical technique.

[0136] The particle sizes (major axial diameters) corresponding to the number of particles of 50 % and 84.13 %, respectively, were read from the graph, and the geometrical standard deviation was calculated from the following formula:

Geometrical standard deviation =

{particle size (major axial diameters)

corresponding to 84.13 % under integration

sieve}/{particle size (major axial diameters)

(geometrical average diameter) corresponding

to 50 % under integration sieve}

[0137] The closer to 1 the geometrical standard deviation value, the more excellent the particle size distribution.

(4) The specific surface area was expressed by the value measured by a BET method.

(5) The amounts of Al and Si which were present within black magnetic composite particles or on surfaces thereof, and the amount of Si contained in the organosilicon compounds, were measured by a fluorescent X-ray spectroscopy device 3063 (manufactured by Rigaku Denki Kogyo Co., Ltd.) according to JIS K0119 "General rule of fluorescent X-ray analysis".

(6) The amount of carbon adhered on the black magnetic composite particles was measured by "Horiba Metal, Carbon and Sulfur Analyzer EMIA-2200 Model" (manufactured by Horiba Seisakusho Co., Ltd.).

(7) The fluidity of magnetic iron oxide particles, black magnetic composite particles and magnetic toner was expressed by a fluidity index which was a sum of indices obtained by converting on the basis of the same reference measured values of an angle of repose, a degree of compaction (%), an angle of spatula and a degree of agglomeration as particle characteristics which were measured by a powder tester (tradename, produced by Hosokawa Micron Co., Ltd.). The closer to 100 the fluidity index, the more excellent the fluidity of the particles.

(8) The blackness of magnetic iron oxide particles, black magnetic composite particles and magnetic toner was measured by the following method. That is, 0.5 g of sample particles and 1.5 cc of castor oil were intimately kneaded together by a Hoover's muller to form a paste. 4.5 g of clear lacquer was added to the obtained paste and was intimately kneaded to form a paint. The obtained paint was applied on a cast-coated paper by using a 6-mil applicator to produce a coating film piece (having a film thickness of about 30 μm). The thus obtained coating film piece was measured according to JIS Z 8729 by a multi-light source spectrographic colorimeter MSC-IS-2D (manufactured by Suga Testing Machines Manufacturing Co., Ltd.) to determine an L* value of colorimetric indices thereof. The blackness was expressed by the L* value measured.

Here, the L* value represents a lightness, and the smaller the L* value, the more excellent the blackness.

(9) The desorption percentage of carbon black fine particles adhered on the black magnetic composite particles was measured by the following method. The closer to zero the desorption percentage, the smaller the amount of carbon black fine particles desorbed from the surfaces of black magnetic composite particles.

That is, 3 g of the black magnetic composite particles and 40 ml of ethanol were placed in a 50-ml precipitation pipe and then was subjected to ultrasonic dispersion for 20 minutes. Thereafter, the obtained dispersion was allowed to stand for 120 minutes, and the carbon black fine particles desorbed were separated from the black magnetic composite particles on the basis of the difference in specific gravity between both the particles. Next, the black magnetic composite particles from which the desorbed carbon black fine particles were separated, were mixed again with 40 ml of ethanol, and the obtained mixtur was furth r subject d to ultrasonic dispersion for 20 minut s. Ther after, th obtained dispersion was allowed to stand for 120 minutes, thereby separating the black magnetic composit particles and the desorbed carbon black desorbed from ach other. The thus obtained black magn tic composit particl s were dried at 100°C for one hour, and then the carbon content thereof was measured by the "Horiba Metal, Carbon and Sulfur Analyzer EMIA-2200 Model" (manufactured by Horiba Seisakusho Co., Ltd.). The desorption percentage of the carbon black fin particl s was calculated according to the following for-

mula:

$$\text{Desorption percentage of carbon black fine particles} = \{(W_a - W_e)/W_a\} \times 100$$

wherein W_a represents an amount of carbon black fine particles initially adhered on the black magnetic composite particles; and W_e represents an amount of carbon black fine particles still adhered on the black magnetic composite particles after desorption test.

(10) The dispersibility in a binder resin of the black magnetic composite particles was evaluated by counting the number of undispersed agglomerated particles on a micrograph (x 200 times) obtained by photographing a sectional area of the obtained black magnetic toner particle using an optical microscope (BH-2, manufactured by Olympus Kogaku Kogyo Co., Ltd.), and classifying the results into the following five ranks. The 5th rank represents the most excellent dispersing condition.

Rank 1: not less than 50 undispersed agglomerated particles per 0.25 mm^2 were recognized;
Rank 2: 10 to 49 undispersed agglomerated particles per 0.25 mm^2 were recognized;
Rank 3: 5 to 9 undispersed agglomerated particles per 0.25 mm^2 were recognized;
Rank 4: 1 to 4 undispersed agglomerated particles per 0.25 mm^2 were recognized;
Rank 5: No undispersed agglomerated particles were recognized.

(11) The average particle size of the black magnetic toner was measured by a laser diffraction-type particle size distribution-measuring apparatus (Model HELOSLA/KA, manufactured by Sympatec Corp.).

(12) The volume resistivity of the magnetic iron oxide particles, the black magnetic composite particles and the black magnetic toner was measured by the following method.

That is, first, 0.5 g of a sample particles or toner to be measured was weighted, and press-molded at 140 Kg/cm^2 using a KBr tablet machine (manufactured by Simazu Seisakusho Co., Ltd.), thereby forming a cylindrical test piece.

Next, the thus obtained cylindrical test piece was exposed to an atmosphere maintained at a temperature of 25°C and a relative humidity of 60 % for 12 hours. Thereafter, the cylindrical test piece was set between stainless steel electrodes, and a voltage of 15V was applied between the electrodes using a Wheatstone bridge (TYPE2768, manufactured by Yokogawa-Hokushin Denki Co., Ltd.) to measure a resistance value R (Ω).

The cylindrical test piece was measured with respect to an upper surface area A (cm^2) and a thickness t_0 (cm) thereof. The measured values were inserted into the following formula, thereby obtaining a volume resistivity X (Ω•cm).

$$X\ (\Omega\cdot cm) = R \times (A/t_0)$$

(13) The magnetic properties of the magnetic iron oxide particles and the black magnetic composite particles were measured using a vibration sample magnetometer "VSM-3S-15" (manufactured by Toei Kogyo Co., Ltd.) by applying an external magnetic field of 10 kOe thereto. Whereas, the magnetic properties of the black magnetic toner were measured by applying external magnetic fields of 1 kOe and 10 kOe thereto.

Example 1:

<Production of black magnetic composite particles>

[0138] 20 kg of spherical magnetite particl s shown in the electron micrograph (× 20,000) of Fig. 1 (averag particle siz : 0.23 μm; geometrical standard deviation value: 1.42; BET specific surface area value: 9.2 m^2/g; blackness (L* value): 20.6; fluidity index: 35; coercive force valu : 61 Oe; saturation magn tization value in a magnetic field of 10 kOe: 84.9 emu/g; residual magnetization value in a magnetic field of 10 kOe: 7.8 emu/g), were deagglomerated in 150 liters of pur water using a stirrer, and further pass d through a "TK pipelin homomix r" (tradename, manufactured by Tokushu Kika Kogyo Co., Ltd.) three times, ther by obtaining a slurry containing the spherical magnetite particl s.

[0139] Successively, the obtained slurry containing the spherical magnetite particles was pass d through a transverse-type sand grinder (tradename "MIGHTY MILL MHG-1.5L", manufactured by Inoue Seisakusho Co., Ltd.) five times at an axis-rotating speed of 2,000 rpm, ther by obtaining a slurry in which the spherical magnetit particles w re dispersed.

[0140] The particles in the obtained slurry which remained on a sieve of 325 meshes (mesh size: 44 μm) was 0 %. The slurry was filtered and washed with water, thereby obtaining a filter cake containing the spherical magnetite particles. After the obtained filter cake containing the spherical magnetite particles was dried at 120°C, 11.0 kg of the dried particles were then charged into an edge runner "MPUV-2 Model" (tradename, manufactured by Matsumoto Chuzo Tekkosho Co., Ltd.), and mixed and stirred at 30 Kg/cm for 30 minutes, thereby lightly deagglomerating the particles.

[0141] 110 g of methyl triethoxysilane was mixed and diluted with 200 ml of ethanol to obtain a methyl triethoxysilane solution. The methyl triethoxysilane solution was added to the deagglomerated spherical magnetite particles under the operation of the edge runner. The spherical magnetite particles were continuously mixed and stirred at a linear load of 60 Kg/cm for 60 minutes.

[0142] Next, 990 g of carbon black fine particles shown in the electron micrograph (× 20,000) of Fig. 2 (particle shape: granular shape; average particle size: 0.022 μm; geometrical standard deviation value: 1.68; BET specific surface area value: 134 m^2/g; and blackness (L^* value): 16.6) were added to the spherical magnetite particles coated with methyl triethoxysilane for 10 minutes while operating the edge runner. Further, the mixed particles were continuously stirred at a linear load of 60 Kg/cm for 60 minutes to adhere the carbon black fine particles on the coating composed of methyl triethoxysilane, thereby obtaining black magnetic composite particles.

[0143] The obtained black magnetic composite particles were aged at 105°C for 60 minutes by using a drier to evaporate water, ethanol or the like which were remained on surfaces of the composite particles. As shown in the electron micrograph (× 20,000) of Fig. 3, the resultant black magnetic composite particles had an average particle size of 0.24 μm. In addition, the black magnetic composite particles showed a geometrical standard deviation value of 1.42, a BET specific surface area value of 10.2 m^2/g, a fluidity index of 46 and a blackness (L^* value) of 18.5. The desorption percentage of the carbon black fine particles from the black magnetic composite particles was 7.5 %. As to the magnetic properties, the coercive force value of the black magnetic composite particles was 61 Oe; the saturation magnetization value in a magnetic field of 10 kOe was 77.3 emu/g; and the residual magnetization value in a magnetic field of 10 kOe was 7.1 emu/g. The coating amount of an organosilane compound produced from methyl triethoxysilane was 0.31 % by weight calculated as Si. Since no independent carbon black fine particles were observed on the electron micrograph of Fig. 3, it was determined that a whole amount of the carbon black fine particles were adhered on the coating composed of the organosilane compound produced from methyl triethoxysilane.

Example 2:

<Production of black magnetic toner containing black magnetic composite particles>

[0144] 400 g of the black magnetic composite particles obtained in Example 1, 540 g of styrene-butyl acrylate-methyl methacrylate copolymer resin (molecular weight = 130,000, styrene/butyl acrylate/methyl methacrylate = 82.0/16.5/1.5), 60 g of polypropylene wax (molecular weight: 3,000) and 15 g of a charge-controlling agent were charged into a Henschel mixer, and mixed and stirred therein at 60°C for 15 minutes. The obtained mixed particles were melt-kneaded at 140°C using a continuous-type twin-screw kneader (T-1), and the obtained kneaded material was cooled, coarsely pulverized and finely pulverized in air. The obtained particles were subjected to classification, thereby producing a black magnetic toner.

[0145] The obtained black magnetic toner had an average particle size of 9.7 μm, a dispersibility of 5th rank, a fluidity index of 73, a blackness (L^* value) of 18.3, a volume resistivity of 1.0×10^{14} Ω•cm, a coercive force value of 60 Oe, a saturation magnetization value (in a magnetic field of 10 kOe) of 32.6 emu/g, a residual magnetization value (in a magnetic field of 10 kOe) of 4.3 emu/g, a saturation magnetization value (in a magnetic field of 1 kOe) of 25.9 emu/g, and a residual magnetization value (in a magnetic field of 1 kOe) of 3.5 emu/g.

Example 3:

<Production of black magnetic composite particles>

[0146] 20 kg of spherical magnetite particles shown in the electron micrograph (× 20,000) of Fig. 1 (av rage particle size: 0.23 μm; geometrical standard d viation value: 1.42; BET specific surface ar a value: 9.2 m^2/g; blackness (L^* value): 20.6; fluidity ind x: 35; coerciv force value: 61 Oe; saturation magnetization valu in a magnetic field of 10 kOe: 84.9 emu/g; residual magnetization valu in a magnetic fi ld of 10 kO : 7.8 emu/g), w r deagglomerated in 150 liters of pure water using a stirrer, and furth r passed through a "TK pipeline homomixer" (tradenam , manufactured

by Tokushu Kika Kogyo Co., Ltd.) three times, thereby obtaining a slurry containing the sph rical magn tite particles.

[0147] Successiv ly, the obtain d slurry containing the spherical magnetite particles was passed through a transverse-type sand grind r (trad name "MIGHTY MILL MHG-1.5L", manufactured by Inoue S isakusho Co., Ltd.) five times at an axis-rotating speed of 2,000 rpm, thereby obtaining a slurry in which the spherical magnetit particles were dispersed.

[0148] The particles in the obtained slurry which remained on a sieve of 325 meshes (mesh size: 44 μm) was 0 %. The slurry was filtered and washed with water, thereby obtaining a filter cake containing the spherical magnetite particles. After the obtained filter cake containing the spherical magnetite particles was dried at 120°C, 11.0 kg of the dried particles were then charged into an edge runner "MPUV-2 Model" (tradename, manufactured by Matsumoto Chuzo Tekkosho Co., Ltd.), and mixed and stirred at 30 Kg/cm for 30 minutes, thereby lightly deagglomerating the particles.

[0149] 110 g of methyl hydrogen polysiloxane (tradename: "TSF484", produced by TOSHIBA SILICONE CO., LTD.) were added to the deagglomerated spherical magnetite particles under the operation of the edge runner. The spherical magnetite particles were continuously mixed and stirred at a linear load of 60 Kg/cm for 60 minutes.

[0150] Next, 990 g of carbon black fine particles shown in the electron micrograph (× 20,000) of Fig. 2 (particle shape: granular shape; average particle size: 0.022 μm; geometrical standard deviation value: 1.68; BET specific surface area value: 134 m^2/g; and blackness (L* value): 16.6) were added to the spherical magnetite particles coated with methyl hydrogen polysiloxane for 10 minutes while operating the edge runner. Further, the mixed particles were continuously stirred at a linear load of 60 Kg/cm for 60 minutes to adhere the carbon black fine particles on the coating composed of methyl hydrogen polysiloxane, thereby obtaining black magnetic composite particles.

[0151] The obtained black magnetic composite particles were dried at 105°C for 60 minutes by using a drier to evaporate water or the like which were remained on surfaces of the composite particles. The obtained black magnetic composite particles had an average particle size of 0.24 μm. In addition, the black magnetic composite particles had a geometrical standard deviation value of 1.42, a BET specific surface area value of 9.8 m^2/g, a fluidity index of 48 and a blackness (L* value) of 18.2. The desorption percentage of the carbon black fine particles from the black magnetic composite particles was 6.5 %. As to the magnetic properties, the coercive force value of the black magnetic composite particles was 59 Oe; the saturation magnetization value in a magnetic field of 10 kOe was 76.8 emu/g; and the residual magnetization value in a magnetic field of 10 kOe was 7.0 emu/g. The coating amount of methyl hydrogen polysiloxane was 0.44 % by weight calculated as Si. Since no independent carbon black fine particles were observed on the electron micrograph, it was determined that a whole amount of the carbon black fine particles were adhered on the coating composed of methyl hydrogen polysiloxane.

Example 4:

<Production of black magnetic toner containing black magnetic composite particles>

[0152] 400 g of the black magnetic composite particles obtained in Example 3, 540 g of styrene-butyl acrylate-methyl methacrylate copolymer resin (molecular weight = 130,000, styrene/butyl acrylate/methyl methacrylate = 82.0/16.5/1.5), 60 g of polypropylene wax (molecular weight: 3,000) and 15 g of a charge-controlling agent were charged into a Henschel mixer, and mixed and stirred therein at 60°C for 15 minutes. The obtained mixed particles were melt-kneaded at 140°C using a continuous-type twin-screw kneader (T-1), and the obtained kneaded material was cooled, coarsely pulverized and finely pulverized in air. The obtained particles were subjected to classification, thereby producing a black magnetic toner.

[0153] The obtained black magnetic toner had an average particle size of 9.7 μm, a dispersibility of 5th rank, a fluidity index of 72, a blackness (L* value) of 18.1, a volume resistivity of 1.2×10^{14} Ω•cm, a coercive force value of 59 Oe, a saturation magnetization value (in a magnetic field of 10 kOe) of 32.4 emu/g, a residual magnetization value (in a magnetic field of 10 kOe) of 4.1 emu/g, a saturation magnetization value (in a magnetic field of 1 kOe) of 25.7 emu/g, and a residual magnetization value (in a magnetic field of 1 kOe) of 3.4 emu/g.

Example 5:

<Production of black magnetic composite particles>

[0154] 20 kg of spherical magnetit particl s shown in the electron micrograph (× 20,000) of Fig. 1 (av rage particle siz : 0.23 μm; geometrical standard deviation value: 1.42; BET specific surface area value: 9.2 m^2/g; blackness (L* valu): 20.6; fluidity index: 35; coercive forc value: 61 Oe; saturation magnetization valu in a magnetic fi ld of 10 kOe: 84.9 emu/g; residual magnetization value in a magn tic field of 10 kOe: 7.8 emu/g), were deagglomerat d in 150 liters of pure water using a tirr r, and furth r passed through a "TK pipelin homomixer" (tradename, manufactur d by Tokushu Kika Kogyo Co., Ltd.) three times, thereby btaining a slurry containing the sph rical magnetite particles.

[0155] Successively, the obtained slurry containing the spherical magnetite particles was passed through a transverse-type sand grinder (tradename "MIGHTY MILL MHG-1.5L", manufactured by Inoue Seisakusho Co., Ltd.) five times at an axis-rotating speed of 2,000 rpm, thereby obtaining a slurry in which the spherical magnetite particles were dispersed.

[0156] The particles in the obtained slurry which remained on a sieve of 325 meshes (mesh size: 44 µm) was 0 %. The slurry was filtered and washed with water, thereby obtaining a filter cake containing the spherical magnetite particles. After the obtained filter cake containing the spherical magnetite particles was dried at 120°C, 11.0 kg of the dried particles were then charged into an edge runner "MPUV-2 Model" (tradename, manufactured by Matsumoto Chuzo Tekkosho Co., Ltd.), and mixed and stirred at 30 Kg/cm for 30 minutes, thereby lightly deagglomerating the particles.

[0157] 220 g of tridecafluorooctyl trimethoxysilane (tradename "TSL8257", produced by TOSHIBA SILICONE CO., LTD.) were added to the deagglomerated spherical magnetite particles under the operation of the edge runner. The spherical magnetite particles were continuously mixed and stirred at a linear load of 60 Kg/cm for 60 minutes.

[0158] Next, 990 g of carbon black fine particles shown in the electron micrograph (× 20,000) of Fig. 2 (particle shape: granular shape; average particle size: 0.022 µm; geometrical standard deviation value: 1.68; BET specific surface area value: 134 m^2/g; and blackness (L* value): 16.6) were added to the spherical magnetite particles coated with tridecafluorooctyl trimethoxysilane for 10 minutes while operating the edge runner. Further, the mixed particles were continuously stirred at a linear load of 60 Kg/cm for 60 minutes to adhere the carbon black fine particles on the coating composed of tridecafluorooctyl trimethoxysilane, thereby obtaining black magnetic composite particles.

[0159] The obtained black magnetic composite particles were aged at 105°C for 60 minutes by using a drier to evaporate water or the like which were remained on surfaces of the composite particles. The obtained black magnetic composite particles had an average particle size of 0.24 µm. In addition, the black magnetic composite particles showed a geometrical standard deviation value of 1.42, a BET specific surface area value of 8.6 m^2/g, a fluidity index of 48 and a blackness (L* value) of 18.4. The desorption percentage of the carbon black fine particles from the black magnetic composite particles was 6.8 %. As to the magnetic properties, the coercive force value of the black magnetic composite particles was 61 Oe; the saturation magnetization value in a magnetic field of 10 kOe was 76.8 emu/g; and the residual magnetization value in a magnetic field of 10 kOe was 6.9 emu/g. The coating amount of a fluorine-containing organosilane compound produced from tridecafluorooctyl trimethoxysilane was 0.13 % by weight calculated as Si. Since no independent carbon black fine particles were observed on the electron micrograph, it was determined that a whole amount of the carbon black fine particles were adhered on the coating composed of the fluorine-containing organosilane compound produced from tridecafluorooctyl trimethoxysilane.

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Example 6:

<Production of black magnetic toner containing black magnetic composite particles>

[0160] 400 g of the black magnetic composite particles obtained in Example 5, 540 g of styrene-butyl acrylate-methyl methacrylate copolymer resin (molecular weight = 130,000, styrene/butyl acrylate/methyl methacrylate = 82.0/16.5/1.5), 60 g of polypropylene wax (molecular weight: 3,000) and 15 g of a charge-controlling agent were charged into a Henschel mixer, and mixed and stirred therein at 60°C for 15 minutes. The obtained mixed particles were melt-kneaded at 140°C using a continuous-type twin-screw kneader (T-1), and the obtained kneaded material was cooled, coarsely pulverized and finely pulverized in air. The obtained particles were subjected to classification, thereby producing a black magnetic toner.

[0161] The obtained black magnetic toner had an average particle size of 10.1 µm, a dispersibility of 5th rank, a fluidity index of 75, a blackness (L* value) of 18.5, a volume resistivity of 1.3×10^{14} Ω•cm, a coercive force value of 58 Oe, a saturation magnetization value (in a magnetic field of 10 kOe) of 32.4 emu/g, a residual magnetization value (in a magnetic field of 10 kOe) of 4.2 emu/g, a saturation magnetization value (in a magnetic field of 1 kOe) of 25.7 emu/g, and a residual magnetization value (in a magnetic field of 1 kOe) of 3.4 emu/g.

Core particles 1 to 4:

[0162] Various magnetic iron oxide particles were prepared by known methods. The same procedure as defined in Example 1 was conducted by using the thus prepared particles, thereby obtaining deagglomerated magnetic iron oxide particles as core particles.

[0163] Various properties of the thus obtained magnetic iron oxide particles are shown in Table 1.

Core particles 5:

[0164] The same procedure as defined in Example 1 was conducted by using 20 kg of the deagglomerated octahedral

magnetite particles (core particl s 1) and 150 liters of water, thereby obtaining a slurry containing the octah dral magnetite particles. Th pH value of th obtained re-dispersed slurry containing th octah dral magnetite particles was adjusted to 4.0, and then the conc ntration of the slurry was adjusted to 98 g/liter by adding water thereto. After 150 liters of th slurry was h ated to 60°C, 2722 ml of a 1.0 mol/lit r aluminum sulfate solution (equivalent to 1.0 % by weight (calculated as Al) based on the weight of the octahedral magnetite particles) was added to the slurry. After allowing the slurry to stand for 30 minutes, the pH value of the slurry was adjusted to 7.5 by adding an aqueous sodium hydroxide solution. Successively, 254 g of water glass #3 (equivalent to 0.5 % by weight (calculated as SiO_2) based on the weight of the octahedral magnetite particles) was added to the slurry. After the slurry was aged for 30 minutes, the pH value of the slurry was adjusted to 7.5 by adding acetic acid. After further allowing the slurry to stand for 30 minutes, the slurry was subjected to filtration, washing with water, drying and pulverization, thereby obtaining the octahedral magnetite particles coated with hydroxides of aluminum and oxides of silicon.

[0165] Main production conditions are shown in Table 2, and various properties of the obtained octahedral magnetite particles are shown in Table 3.

Core particles 6 to 8:

[0166] The same procedure as defined in the production of the core particles 5 above, was conducted except that kind of core particles, and kind and amount of additives used in the surface treatment were varied, thereby obtaining surface-treated magnetic iron oxide particles.

[0167] Main production conditions are shown in Table 2, and various properties of the obtained surface-treated magnetic iron oxide particles are shown in Table 3.

Examples 7 to 14 and Comparative Examples 1 to 5:

[0168] The same procedure as defined in Example 1 was conducted except that kind of particles to be treated, addition or non-addition of an alkoxysilane compound in the coating treatment with alkoxysilane compound, kind and amount of the alkoxysilane compound added, treating conditions of edge runner in the coating treatment, kind and amount of carbon black fine particles adhered, and treating conditions of edge runner used in the adhering process of the carbon black fine particles, were varied, thereby obtaining black magnetic composite particles. The black magnetic composite particles obtained in Examples 7 to 14 were observed by an electron microscope. As a result, almost no independent carbon black fine particles were recognized. Therefore, it was confirmed that a substantially whole amount of the carbon black fine particles were adhered on the coating composed of organosilane compound produced from the alkoxysilane compound.

[0169] Various properties of the carbon black fine particles A to C are shown in Table 4.

[0170] Main production conditions are shown in Table 5, and various properties of the obtained black magnetic composite particles are shown in Table 6.

[0171] Meanwhile, in Comparative Example 1, the spherical magnetite particles uncoated with the alkoxysilane compound and the carbon black fine particles were mixed and stirred together by an edge runner in the same manner as described above, thereby obtaining treated particles. An electron micrograph (× 20,000) of the thus treated particles is shown in Fig. 4. As shown in Fig. 4, it was confirmed that the carbon black fine particles were not adhered on the surfaces of the spherical magnetite particles, and both the particles were present independently.

Examples 15 to 22 and Comparative Examples 6 to 14:

<Production of black magnetic toner>

[0172] The same procedure as defined in Example 2 was conducted by using the black magnetic composite particles obtained in Examples 7 to 14, the magnetic iron oxide particles as core particles 1 to 4, the mixed particles composed of the magnetic iron oxide particles and the carbon black fine particles used in Comparative Example 1 and the black magnetic composite particles obtained in Comparative Examples 2 to 5, thereby obtaining black magnetic toners.

[0173] Main production conditions and various properties of the obtained black magnetic toners are shown in Tables 7 and 8.

Examples 23 to 46 and Comparative Examples 15 to 23:

[0174] The same procedure as defined in Example 3 was conducted exc pt that kind of particles to be treated, addition or non-addition of a polysiloxane or modified polysiloxane, kind and amount of th polysiloxane or modifi d polysiloxane, treating conditions of edg runn r in the coating tr atment, kind and amount of carbon black fine particles

adhered, and tr ating conditions of edg runner us d in the adhering process of the carbon black fin particles, w re varied, thereby obtaining black magnetic composite particles. Th black magnetic composite particles obtained in Examples 23 to 46 wer observ d by an l ctron microscop . As a result, almost no independent carbon black fine particles were recognized. Th refore, it was confirmed that a substantially whole amount of the carbon black fine particles were adhered on the coating composed of polysiloxane or modified polysiloxane.

[0175] Main production conditions are shown in Tables 9 to 11, and various properties of the obtained black magnetic composite particles are shown in Tables 12 to 14.

Examples 47 to 70 and Comparative Examples 24 to 32:

<Production of black magnetic toner>

[0176] The same procedure as defined in Example 4 was conducted by using the black magnetic composite particles obtained in Examples 47 to 70, and the black magnetic composite particles obtained in Comparative Examples 15 to 23, thereby obtaining black magnetic toners.

[0177] Main production conditions and various properties of the obtained black magnetic toners are shown in Tables 15 to 17.

Examples 71 to 78 and Comparative Examples 33 to 35:

[0178] The same procedure as defined in Example 5 was conducted except that kind of particles to be treated, addition or non-addition of a fluoroalkyl organosilane compound, kind and amount of the fluoroalkyl organosilane compound added, treating conditions of edge runner in the coating treatment, kind and amount of carbon black fine particles adhered, and treating conditions of edge runner used in the adhering process of the carbon black fine particles, were varied, thereby obtaining black magnetic composite particles. The black magnetic composite particles obtained in Examples 71 to 78 were observed by an electron microscope. As a result, almost no independent carbon black fine particles were recognized. Therefore, it was confirmed that a substantially whole amount of the carbon black fine particles were adhered on the coating composed of a fluorine-containing organosilane compound produced from the fluoroalkyl organosilane compound.

[0179] Main production conditions are shown in Table 18, and various properties of the obtained black magnetic composite particles are shown in Table 19.

Examples 79 to 86 and Comparative Examples 36 to 38:

<Production of black magnetic toner>

[0180] The same procedure as defined in Example 6 was conducted by using the black magnetic composite particles obtained in Examples 71 to 78, and the black magnetic composite particles obtained in Comparative Examples 33 to 35, thereby obtaining black magnetic toners.

[0181] Main production conditions and various properties of the obtained black magnetic toners are shown in Table 20.

Table 1

Core particles	Properties of magnetic iron oxide particles				
	Kind	Particle shape	Average particle size (μm)	Aspect ratio (-)	Geometrical standard deviation (-)
Core particles 1	Magnetite particles	Octahedral	0.28	-	1.53
Core particles 2	Magnetite particles	Spherical	0.23	-	1.35
Core particles 3	Magnetite particles	Acicular	0.40	8.1:1	1.53
Core particles 4	Maghemite particles	Spherical	0.20	-	1.42

Table 1 (continued)

Core particles	Properties of magnetic iron oxide particles					
	BET specific surface area (m^2/g)	Magnetic properties			Fluidity index (-)	Blackness (L* value) (-)
		Coercive force (Oe)	Saturation magnetization (10kOe) (emu/g)	Residual magnetization (10kOe) (emu/g)		
Core particles 1	4.6	101	86.8	12.2	34	20.3
Core particles 2	11.8	63	85.1	7.7	38	20.1
Core particles 3	18.8	343	86.3	29.3	32	23.8
Core particles 4	7.2	54	78.8	8.7	38	31.5

Table 2

Core particles	Kind of core particles	Surface-treating process		
		Additives		
		Kind	Calculated as	Amount (wt. %)
Core particles 5	Core particles 1	Aluminum sulfate Water glass #3	Al SiO_2	1.0 0.5
Core particles 6	Core particles 2	Sodium aluminate Colloidal silica	Al SiO_2	2.0 1.0
Core particles 7	Core particles 3	Aluminum acetate	Al	5.0
Core particles 8	Core particles 4	Water glass #3	SiO_2	1.0

Table 2 (continued)

Core particles	Surface-treating process		
	Coating material		
	Kind	Calculated as	Amount (wt. %)
Core particles 5	A S	Al SiO_2	0.98 0.49
Core particles 6	A S	Al SiO_2	1.92 0.96
Core particles 7	A	Al	4.75
Core particles 8	S	SiO_2	0.98

Note; A: Hydroxide of aluminum
S: Oxide of silicon

Table 3

Core particles	Properties of surface-treated magnetic iron oxide particles			
	Average particle size (μm)	Aspect ratio (-)	Geometrical standard deviation (-)	BET specific surface area (m^2/g)
Core particles 5	0.29	-	1.51	9.8
Core particles 6	0.24	-	1.35	13.6
Core particles 7	0.40	8.1:1	1.52	25.4
Core particles 8	0.20	-	1.42	7.5

Table 3 (continued)

Core particles	Properties of surface-treated magnetic iron oxide particles				
	Magnetic properties				
	Coercive force (Oe)	Saturation magnetization (10kOe) (emu/g)	Residual magnetization (10kOe) (emu/g)	Fluidity index (-)	Blackness (L* value) (-)
Core particles 5	103	86.3	12.1	32	21.4
Core particles 6	62	84.8	7.6	37	20.8
Core particles 7	336	86.0	19.8	32	24.6
Core particles 8	53	78.6	8.6	37	31.6

Table 4

Kind of carbon black fine particles	Properties of carbon black fine particles		
	Particle shape	Average particle size (µm)	Geometrical standard deviation (-)
Carbon black A	Granular	0.022	1.78
Carbon black B	Granular	0.015	1.56
Carbon black C	Granular	0.030	2.06

Table 4 (continued)

Kind of carbon black fine particles	Properties of carbon black fine particles	
	BET specific surface area (m^2/g)	Blackness (L^* value) (-)
Carbon black A	133.5	14.6
Carbon black B	265.3	15.2
Carbon black C	84.6	17.0

Table 5

Examples and Comparative Examples	Kind of particles to be treated	Production of black magnetic composite particles	
		Coating step with alkoxysilane or silicon compound	
		Alkoxysilane compound	
		Kind	Amount added (part by weight)
Example 7	Core particles 1	Dimethyl dimethoxysilane	1.0
Example 8	Core particles 2	Phenyl triethoxysilane	0.5
Example 9	Core particles 3	Isobutyl trimethoxysilane	5.0
Example 10	Core particles 4	Methyl triethoxysilane	1.5
Example 11	Core particles 5	Dimethyl dimethoxysilane	0.2
Example 12	Core particles 6	Phenyl triethoxysilane	1.5
Example 13	Core particles 7	Isobutyl trimethoxysilane	1.0
Example 14	Core particles 8	Methyl triethoxysilane	2.0
Comparative Example 1	Core particles used in Example 1	-	-
Comparative Example 2	Core particles 1	Methyl triethoxysilane	1.0
Comparative Example 3	Core particles 1	Dimethyl dimethoxysilane	0.5
Comparative Example 4	Core particles 1	Methyl triethoxysilane	0.005
Comparative Example 5	Core particles 1	γ-aminopropyl triethoxysilane	1.0

Table 5 (continued)

Examples and Comparative Examples	Production of black magnetic composite particles		
	Coating step with alkoxysilane or silicon compound		
	Edge runner treatment		Coating amount (calculated as Si) (wt. %)
	Linear load (Kg/cm)	Time (min)	
Example 7	45	15	0.22
Example 8	75	20	0.06
Example 9	30	60	0.73
Example 10	60	30	0.24
Example 11	60	20	0.05
Example 12	30	60	0.18
Example 13	45	30	0.16
Example 14	60	30	0.32
Comparative Example 1	-	-	-
Comparative Example 2	30	60	0.21
Comparative Example 3	60	30	0.11
Comparative Example 4	60	30	7.9×10^{-4}
Comparative Example 5	60	60	0.126

Table 5 (continued)

Examples and Comparative Examples	Production of black magnetic composite particles	
	Adhering step of carbon black fine particles	
	Carbon black fine particles	
	Kind	Amount added (part by weight)
Example 7	B	6.0
Example 8	B	12.0
Example 9	C	16.0
Example 10	A	25.0
Example 11	B	20.0
Example 12	B	15.0
Example 13	C	10.0
Example 14	A	20.0
Comparative Example 1	Carbon black fine particles used in Example 1	10.0
Comparative Example 2	-	-
Comparative Example 3	A	0.01
Comparative Example 4	B	5.0
Comparative Example 5	C	7.0

Table 5 (continued)

Examples and Comparative Examples	Production of black magnetic composite particles		
	Adhering step of carbon black fine particles		
	Edge runner treatment		Amount adhered (calculated as C) (wt. %)
	Linear load (Kg/cm)	Time (min)	
Example 7	30	60	5.66
Example 8	30	90	10.73
Example 9	45	45	13.70
Example 10	60	60	22.65
Example 11	30	45	16.63
Example 12	60	60	12.99
Example 13	60	30	9.09
Example 14	75	30	17.09
Comparative Example 1	60	30	9.06
Comparative Example 2	-	-	-
Comparative Example 3	30	60	0.01
Comparative Example 4	60	45	4.75
Comparative Example 5	60	30	2.88

Table 6

Examples and Comparative Examples	Properties of black magnetic composite particles			
	Average particle size (μm)	Aspect ratio (-)	Geometrical standard deviation (-)	BET specific surface area (m^2/g)
Example 7	0.28	-	1.52	5.0
Example 8	0.24	-	1.34	13.6
Example 9	0.41	8.1:1	1.51	23.8
Example 10	0.23	-	1.43	15.3
Example 11	0.30	-	1.47	14.4
Example 12	0.24	-	1.34	16.1
Example 13	0.40	8.0:1	1.50	24.8
Example 14	0.23	-	1.42	13.8
Comparative Example 1	0.29	-	1.53	11.9
Comparative Example 2	0.29	-	1.52	10.6
Comparative Example 3	0.28	-	1.52	5.6
Comparative Example 4	0.28	-	1.52	17.6
Comparative Example 5	0.29	-	1.52	11.2

Table 6 (continued)

Examples and Comparative Examples	Properties of black magnetic composite particles		
	Magnetic properties		
	Coercive force (Oe)	Saturation magnetization (10 kOe) (emu/g)	Residual magnetization (10 kOe) (emu/g)
Example 7	108	81.1	11.4
Example 8	65	71.8	6.5
Example 9	336	73.8	25.8
Example 10	58	63.6	6.4
Example 11	106	72.8	10.2
Example 12	68	74.1	6.7
Example 13	331	77.8	27.2
Example 14	57	65.6	7.2
Comparative Example 1	103	79.3	10.3
Comparative Example 2	103	83.6	10.8
Comparative Example 3	104	86.7	11.3
Comparative Example 4	100	83.8	10.9
Comparative Example 5	102	84.6	10.6

Table 6 (continued)

Examples and Comparative Examples	Properties of black magnetic composite particles		
	Fluidity index (-)	Blackness (L* value) (-)	Carbon black desorption percentage (%)
Example 7	49	17.0	8.6
Example 8	45	16.4	8.2
Example 9	46	17.8	6.4
Example 10	54	17.5	5.2
Example 11	52	15.9	3.1
Example 12	47	16.2	3.6
Example 13	48	17.5	2.1
Example 14	51	17.9	3.8
Comparative Example 1	42	20.0	78.6
Comparative Example 2	40	20.9	-
Comparative Example 3	38	21.4	31.2
Comparative Example 4	40	20.1	26.5
Comparative Example 5	41	20.6	41.6

Table 7

Examples	Production of black magnetic toner			
	Black magnetic composite particles		Resin	
	Kind	Amount blended (part by weight)	Kind	Amount blended (part by weight)
Example 15	Example 7	45	Styrene-acryl copolymer resin	55
Example 16	Example 8	45	Styrene-acryl copolymer resin	55
Example 17	Example 9	40	Styrene-acryl copolymer resin	60
Example 18	Example 10	50	Styrene-acryl copolymer resin	50
Example 19	Example 11	45	Styrene-acryl copolymer resin	55
Example 20	Example 12	40	Styrene-acryl copolymer resin	60
Example 21	Example 13	50	Styrene-acryl copolymer resin	50
Example 22	Example 14	50	Styrene-acryl copolymer resin	50

Table 7 (continued)

Examples	Properties of black magnetic toner			
	Average particle size (μm)	Dispersibility (-)	Fluidity index (-)	Volume resistivity (Ω•cm)
Example 15	9.6	4	74	9.8×10^{13}
Example 16	10.1	5	82	1.6×10^{14}
Example 17	11.2	4	72	7.3×10^{13}
Example 18	10.6	5	78	8.6×10^{13}
Example 19	9.2	5	78	6.8×10^{13}
Example 20	9.8	5	86	2.6×10^{14}
Example 21	8.9	5	73	1.8×10^{14}
Example 22	11.0	5	82	1.1×10^{14}

Table 7 (continued)

Examples	Properties of black magnetic toner		
	Magnetic properties		
	Coercive force (Oe)	Saturation magnetization	
		(10 kOe) (emu/g)	(1 kOe) (emu/g)
Example 15	96	36.8	27.6
Example 16	61	33.6	26.1
Example 17	311	31.4	23.4
Example 18	56	32.3	22.7
Example 19	103	32.3	23.6
Example 20	66	29.6	22.2
Example 21	320	39.1	29.7
Example 22	53	31.9	23.9

Table 7 (continued)

Examples	Properties of black magnetic toner		
	Magnetic properties		Blackness (L* value) (-)
	Residual magnetization		
	(10 kOe) (emu/g)	(1 kOe) (emu/g)	
Example 15	5.9	4.4	18.7
Example 16	4.0	2.9	18.1
Example 17	11.3	8.5	19.6
Example 18	4.5	3.2	19.2
Example 19	5.2	4.0	17.4
Example 20	3.6	2.7	18.1
Example 21	14.1	9.9	18.9
Example 22	4.5	3.1	19.5

Table 8

Comparative Examples	Production of black magnetic toner			
	Black magnetic particles		Resin	
	Kind	Amount blended (part by weight)	Kind	Amount blended (part by weight)
Comparative Example 6	Core particles 1	45	Styrene-acryl copolymer resin	55
Comparative Example 7	Core particles 2	45	Styrene-acryl copolymer resin	55
Comparative Example 8	Core particles 3	45	Styrene-acryl copolymer resin	55
Comparative Example 9	Core particles 4	45	Styrene-acryl copolymer resin	55
Comparative Example 10	Comparative Example 1	45	Styrene-acryl copolymer resin	55
Comparative Example 11	Comparative Example 2	45	Styrene-acryl copolymer resin	55
Comparative Example 12	Comparative Example 3	45	Styrene-acryl copolymer resin	55
Comparative Example 13	Comparative Example 4	45	Styrene-acryl copolymer resin	55
Comparative Example 14	Comparative Example 5	45	Styrene-acryl copolymer resin	55

Table 8 (continued)

Comparative Examples	Properties of black magnetic toner			
	Average particle size (μm)	Dispersibility (-)	Fluidity index (-)	Volume resistivity (Ω•cm)
Comparative Example 6	10.0	3	60	6.3×10^{12}
Comparative Example 7	10.1	3	65	5.4×10^{12}
Comparative Example 8	9.8	3	58	9.1×10^{11}
Comparative Example 9	10.3	3	63	3.2×10^{12}
Comparative Example 10	11.0	2	55	3.6×10^{11}
Comparative Example 11	10.6	2	58	1.6×10^{12}
Comparative Example 12	10.8	3	61	1.6×10^{12}
Comparative Example 13	10.4	2	58	2.6×10^{12}
Comparative Example 14	10.4	2	57	2.6×10^{12}

Table 8 (continued)

Comparative Examples	Properties of black magnetic toner		
	Magnetic properties		
	Coercive force (Oe)	Saturation magnetization	
		(10 kOe) (emu/g)	(1 kOe) (emu/g)
Comparative Example 6	104	39.6	30.0
Comparative Example 7	61	38.8	29.1
Comparative Example 8	338	37.6	28.8
Comparative Example 9	51	34.6	26.0
Comparative Example 10	99	35.6	26.3
Comparative Example 11	100	39.1	27.1
Comparative Example 12	103	38.1	29.3
Comparative Example 13	102	36.7	28.6
Comparative Example 14	102	36.3	27.8

Table 8 (continued)

Comparative Examples	Properties of black magnetic toner		
	Magnetic properties		Blackness (L* value) (-)
	Residual magnetization		
	(10 kOe) (emu/g)	(1 kOe) (emu/g)	
Comparative Example 6	5.5	4.2	22.3
Comparative Example 7	3.5	2.6	22.1
Comparative Example 8	12.8	9.7	26.0
Comparative Example 9	3.8	3.0	34.8
Comparative Example 10	5.0	3.7	22.6
Comparative Example 11	5.9	4.6	23.3
Comparative Example 12	5.3	4.1	23.5
Comparative Example 13	5.1	3.9	22.3
Comparative Example 14	4.9	3.8	22.1

Table 9

Examples and Comparative Examples	Kind of particles to be treated	Production of black magnetic composite particles	
		Coating step with polysiloxane	
		Polysiloxane	
		Kind	Amount added (part by weight)
Example 23	Core particles 1	TSF484	1.0
Example 24	Core particles 2	TSF484	5.0
Example 25	Core particles 3	KF99	2.0
Example 26	Core particles 4	L-9000	1.0
Example 27	Core particles 5	TSF451	1.5
Example 28	Core particles 6	TSF484	3.5
Example 29	Core particles 7	KF99	1.0
Example 30	Core particles 8	L-9000	2.0
Comparative Example 15	Core particles 1	TSF484	1.0
Comparative Example 16	Core particles 1	TSF484	0.5
Comparative Example 17	Core particles 1	TSF484	0.005

Table 9 (continued)

Examples and Comparative Examples	Production of black magnetic composite particles		
	Coating step with polysiloxane		
	Edge runner treatment		Coating amount (calculated as Si) (wt. %)
	Linear load (Kg/cm)	Time (min)	
Example 23	60	30	0.44
Example 24	45	25	2.18
Example 25	30	30	0.87
Example 26	60	45	0.44
Example 27	45	60	0.62
Example 28	60	30	1.50
Example 29	75	25	0.43
Example 30	60	20	0.87
Comparative Example 15	60	30	0.44
Comparative Example 16	60	30	0.21
Comparative Example 17	60	30	2.2×10^{-3}

Table 9 (continued)

Examples and Comparative Examples	Production of black magnetic composite particles	
	Adhering step of carbon black fine particles	
	Carbon black fine particles	
	Kind	Amount added (part by weight)
Example 23	A	10.0
Example 24	A	3.0
Example 25	B	5.0
Example 26	C	10.0
Example 27	A	5.0
Example 28	A	10.0
Example 29	B	15.0
Example 30	C	10.0
Comparative Example 15	-	-
Comparative Example 16	A	0.01
Comparative Example 17	B	3.0

Table 9 (continued)

Examples and Comparative Examples	Production of black magnetic composite particles		
	Adhering step of carbon black fine particles		
	Edge runner treatment		Amount adhered (calculated as C) (wt. %)
	Linear load (Kg/cm)	Time (min)	
Example 23	60	30	9.05
Example 24	60	45	2.89
Example 25	60	30	4.76
Example 26	45	45	9.12
Example 27	45	30	4.72
Example 28	30	60	8.99
Example 29	60	30	12.89
Example 30	45	25	9.08
Comparative Example 15	-	-	-
Comparative Example 16	60	30	0.01
Comparative Example 17	60	30	2.91

Table 10

Examples and Comparative Examples	Kind of particles to be treated	Production of black magnetic composite particles — Coating step with modified polysiloxane — Modified polysiloxane: Kind	Amount added (part by weight)
Example 31	Core particles 1	BYK-080	1.0
Example 32	Core particles 2	BYK-080	0.5
Example 33	Core particles 3	BYK-310	2.0
Example 34	Core particles 4	BYK-322	5.0
Example 35	Core particles 5	BYK-080	2.0
Example 36	Core particles 6	BYK-080	3.0
Example 37	Core particles 7	BYK-310	1.5
Example 38	Core particles 8	BYK-322	7.0
Comparative Example 18	Core particles 1	BYK-080	1.0
Comparative Example 19	Core particles 1	BYK-080	0.5
Comparative Example 20	Core particles 1	BYK-080	0.005

Table 10 (continued)

Examples and Comparative Examples	Production of black magnetic composite particles		
	Coating step with modified polysiloxane		
	Edge runner treatment		Coating amount (calculated as Si) (wt. %)
	Linear load (Kg/cm)	Time (min)	
Example 31	60	60	0.18
Example 32	30	60	0.08
Example 33	60	45	0.36
Example 34	30	30	0.87
Example 35	45	30	0.36
Example 36	45	45	0.49
Example 37	60	30	0.25
Example 38	30	45	1.20
Comparative Example 18	60	30	0.16
Comparative Example 19	60	30	0.08
Comparative Example 20	60	30	$8.0x10^{-4}$

Table 10 (continued)

Examples and Comparative Examples	Production of black magnetic composite particles	
	Adhering step of carbon black fine particles	
	Carbon black fine particles	
	Kind	Amount added (part by weight)
Example 31	A	8.0
Example 32	A	6.0
Example 33	B	6.5
Example 34	C	11.5
Example 35	A	7.5
Example 36	A	12.5
Example 37	B	18.0
Example 38	C	15.0
Comparative Example 18	-	-
Comparative Example 19	A	0.01
Comparative Example 20	B	5.0

Table 10 (continued)

Examples and Comparative Examples	Production of black magnetic composite particles		
	Adhering step of carbon black fine particles		
	Edge runner treatment		Amount adhered (calculated as C) (wt. %)
	Linear load (Kg/cm)	Time (min)	
Example 31	60	30	7.43
Example 32	30	25	5.68
Example 33	30	30	6.10
Example 34	60	20	10.24
Example 35	45	45	6.98
Example 36	60	30	11.10
Example 37	30	25	15.16
Example 38	45	40	13.10
Comparative Example 18	-	-	-
Comparative Example 19	60	30	0.01
Comparative Example 20	60	30	4.75

Table 11

Examples and Comparative Examples	Kind of particles to be treated	Production of black magnetic composite particles	
		Coating step with terminal-modified polysiloxane	
		Terminal-modified polysiloxane	
		Kind	Amount added (part by weight)
Example 39	Core particles 1	TSF4770	2.0
Example 40	Core particles 2	TSF4770	1.0
Example 41	Core particles 3	TSF4751	0.5
Example 42	Core particles 4	TSF4751	3.0
Example 43	Core particles 5	TSF4770	1.0
Example 44	Core particles 6	TSF4770	3.0
Example 45	Core particles 7	TSF4751	0.5
Example 46	Core particles 8	TSF4751	1.7
Comparative Example 21	Core particles 1	TSF4770	1.0
Comparative Example 22	Core particles 1	TSF4770	1.0
Comparative Example 23	Core particles 1	TSF4770	0.005

Table 11 (continued)

Examples and Comparative Examples	Production of black magnetic composite particles		
	Coating step with terminal-modified polysiloxane		
	Edge runner treatment		Coating amount (calculated as Si) (wt. %)
	Linear load (Kg/cm)	Time (min)	
Example 39	60	30	0.46
Example 40	30	40	0.21
Example 41	60	30	0.12
Example 42	30	45	0.71
Example 43	45	20	0.21
Example 44	60	30	0.69
Example 45	45	20	0.14
Example 46	30	30	0.37
Comparative Example 21	60	30	0.26
Comparative Example 22	60	30	0.25
Comparative Example 23	60	30	$1.2x10^{-3}$

Table 11 (continued)

Examples and Comparative Examples	Production of black magnetic composite particles	
	Adhering step of carbon black fine particles	
	Carbon black fine particles	
	Kind	Amount added (part by weight)
Example 39	A	10.0
Example 40	A	6.0
Example 41	B	8.0
Example 42	C	10.0
Example 43	A	7.5
Example 44	A	12.0
Example 45	B	19.0
Example 46	C	13.0
Comparative Example 21	-	-
Comparative Example 22	A	0.01
Comparative Example 23	B	5.0

Table 11 (continued)

Examples and Comparative Examples	Production of black magnetic composite particles		
	Adhering step of carbon black fine particles		
	Edge runner treatment		Amount adhered (calculated as C) (wt. %)
	Linear load (Kg/cm)	Time (min)	
Example 39	60	30	9.13
Example 40	30	45	5.57
Example 41	45	60	7.42
Example 42	60	45	9.10
Example 43	30	30	6.98
Example 44	45	25	10.70
Example 45	60	45	15.15
Example 46	30	30	11.43
Comparative Example 21	-	-	-
Comparative Example 22	60	30	0.01
Comparative Example 23	60	30	4.73

Table 12

Examples and Comparative Examples	Properties of black magnetic composite particles			
	Average particle size (µm)	Aspect ratio (-)	Geometrical standard deviation (-)	BET specific surface area (m^2/g)
Example 23	0.28	-	1.52	6.1
Example 24	0.24	-	1.34	12.8
Example 25	0.41	8.1:1	1.51	24.6
Example 26	0.23	-	1.42	14.6
Example 27	0.29	-	1.50	14.3
Example 28	0.23	-	1.34	15.1
Example 29	0.40	8.1:1	1.50	24.8
Example 30	0.23	-	1.42	12.8
Comparative Example 15	0.29	-	1.53	11.5
Comparative Example 16	0.28	-	1.53	7.1
Comparative Example 17	0.28	-	1.53	15.6

Table 12 (continued)

Examples and Comparative Examples	Properties of black magnetic composite particles		
	Magnetic properties		
	Coercive force (Oe)	Saturation magnetization (10 kOe) (emu/g)	Residual magnetization (10 kOe) (emu/g)
Example 23	108	80.8	11.0
Example 24	64	71.6	6.6
Example 25	338	75.2	25.8
Example 26	56	64.1	6.3
Example 27	105	73.1	10.1
Example 28	65	75.0	6.3
Example 29	336	77.6	26.5
Example 30	58	65.1	6.8
Comparative Example 15	103	78.6	10.1
Comparative Example 16	104	83.6	10.9
Comparative Example 17	103	83.2	10.6

Table 12 (continued)

Examples and Comparative Examples	Properties of black magnetic composite particles		
	Fluidity index (-)	Blackness (L* value) (-)	Carbon black desorption percentage (%)
Example 23	51	17.0	7.2
Example 24	48	16.5	8.6
Example 25	46	17.2	8.8
Example 26	53	17.4	6.2
Example 27	50	15.3	4.6
Example 28	48	16.0	3.6
Example 29	49	17.6	1.8
Example 30	51	17.6	3.2
Comparative Example 15	39	20.6	60.5
Comparative Example 16	39	21.0	28.3
Comparative Example 17	40	20.8	43.8

Table 13

Examples and Comparative Examples	Properties of black magnetic composite particles			
	Average particle size (μm)	Aspect ratio (-)	Geometrical standard deviation (-)	BET specific surface area (m^2/g)
Example 31	0.28	-	1.52	6.8
Example 32	0.23	-	1.34	11.9
Example 33	0.40	8.1:1	1.52	24.9
Example 34	0.23	-	1.42	13.8
Example 35	0.29	-	1.51	15.1
Example 36	0.23	-	1.34	14.6
Example 37	0.41	8.1:1	1.50	25.6
Example 38	0.23	-	1.42	11.8
Comparative Example 18	0.28	-	1.53	11.3
Comparative Example 19	0.28	-	1.52	10.6
Comparative Example 20	0.28	-	1.53	16.3

Table 13 (continued)

Examples and Comparative Examples	Properties of black magnetic composite particles		
	Magnetic properties		
	Coercive force (Oe)	Saturation magnetization (10 kOe) (emu/g)	Residual magnetization (10 kOe) (emu/g)
Example 31	108	80.6	10.8
Example 32	63	71.8	7.1
Example 33	336	75.3	25.6
Example 34	57	64.6	6.1
Example 35	106	73.2	10.0
Example 36	63	75.2	6.1
Example 37	336	77.8	26.3
Example 38	56	65.3	6.5
Comparative Example 18	102	78.3	10.0
Comparative Example 19	100	83.2	10.8
Comparative Example 20	102	81.6	10.1

Table 13 (continued)

Examples and Comparative Examples	Properties of black magnetic composite particles		
	Fluidity index (-)	Blackness (L* value) (-)	Carbon black desorption percentage (%)
Example 31	52	17.1	8.3
Example 32	52	16.8	9.1
Example 33	53	17.5	6.3
Example 34	46	17.0	5.9
Example 35	48	17.3	4.8
Example 36	51	16.1	3.9
Example 37	50	16.0	3.8
Example 38	53	17.3	2.8
Comparative Example 18	38	21.0	61.3
Comparative Example 19	37	20.6	27.3
Comparative Example 20	38	20.5	45.9

Table 14

Examples and Comparative Examples	Properties of black magnetic composite particles			
	Average particle size (μm)	Aspect ratio (-)	Geometrical standard deviation (-)	BET specific surface area (m^2/g)
Example 39	0.28	-	1.52	5.9
Example 40	0.23	-	1.34	12.6
Example 41	0.41	8.0:1	1.52	25.6
Example 42	0.23	-	1.43	13.9
Example 43	0.29	-	1.50	14.8
Example 44	0.23	-	1.34	16.3
Example 45	0.40	8.1:1	1.50	21.8
Example 46	0.23	-	1.43	13.6
Comparative Example 21	0.29	-	1.52	10.3
Comparative Example 22	0.29	-	1.51	10.6
Comparative Example 23	0.29	-	1.52	10.1

Table 14 (continued)

Examples and Comparative Examples	Properties of black magnetic composite particles		
	Magnetic properties		
	Coercive force (Oe)	Saturation magnetization (10 kOe) (emu/g)	Residual magnetization (10 kOe) (emu/g)
Example 39	107	81.4	11.6
Example 40	66	72.1	6.3
Example 41	341	74.1	25.4
Example 42	59	63.6	6.0
Example 43	107	73.1	10.1
Example 44	66	73.8	6.6
Example 45	340	78.1	26.8
Example 46	56	66.6	6.8
Comparative Example 21	104	83.1	10.0
Comparative Example 22	104	84.1	10.0
Comparative Example 23	103	83.1	10.1

Table 14 (continued)

Examples and Comparative Examples	Properties of black magnetic composite particles		
	Fluidity index (-)	Blackness (L* value) (-)	Carbon black desorption percentage (%)
Example 39	52	16.0	7.1
Example 40	51	16.3	6.5
Example 41	53	17.2	5.9
Example 42	52	17.6	5.3
Example 43	54	16.0	4.3
Example 44	54	16.0	3.4
Example 45	52	17.4	3.8
Example 46	53	17.4	4.3
Comparative Example 21	37	20.8	69.2
Comparative Example 22	37	21.0	31.6
Comparative Example 23	38	20.6	50.8

Table 15

Examples and Comparative Examples	Production of black magnetic toner			
	Black magnetic composite particles		Resin	
	Kind	Amount blended (part by weight)	Kind	Amount blended (part by weight)
Example 47	Example 23	45	Styrene-acryl copolymer resin	55
Example 48	Example 24	45	Styrene-acryl copolymer resin	55
Example 49	Example 25	40	Styrene-acryl copolymer resin	60
Example 50	Example 26	50	Styrene-acryl copolymer resin	50
Example 51	Example 27	45	Styrene-acryl copolymer resin	55
Example 52	Example 28	40	Styrene-acryl copolymer resin	60
Example 53	Example 29	50	Styrene-acryl copolymer resin	50
Example 54	Example 30	50	Styrene-acryl copolymer resin	50
Comparative Example 24	Comparative Example 15	45	Styrene-acryl copolymer resin	55
Comparative Example 25	Comparative Example 16	45	Styrene-acryl copolymer resin	55
Comparative Example 26	Comparative Example 17	45	Styrene-acryl copolymer resin	55

Table 15 (continued)

Examples and Comparative Examples	Properties of black magnetic toner			
	Average particle size (μm)	Dispersibility (-)	Fluidity index (-)	Volume resistivity (Ω•cm)
Example 47	9.9	5	75	8.9×10^{13}
Example 48	10.0	5	81	1.8×10^{14}
Example 49	10.6	4	75	7.6×10^{13}
Example 50	10.5	5	78	7.1×10^{13}
Example 51	9.6	5	79	5.9×10^{13}
Example 52	9.9	5	83	3.1×10^{14}
Example 53	10.0	5	76	1.9×10^{14}
Example 54	10.8	5	83	1.5×10^{14}
Comparative Example 24	10.6	2	56	1.8×10^{12}
Comparative Example 25	10.5	2	58	2.1×10^{12}
Comparative Example 26	10.4	2	56	2.1×10^{12}

Table 15 (continued)

Examples and Comparative Examples	Properties of black magnetic toner		
	Magnetic properties		
	Coercive force (Oe)	Saturation magnetization	
		(10 kOe) (emu/g)	(1 kOe) (emu/g)
Example 47	97	36.6	27.4
Example 48	60	33.4	26.0
Example 49	321	31.4	23.5
Example 50	57	32.3	22.8
Example 51	104	32.5	23.5
Example 52	67	29.8	22.6
Example 53	328	33.6	23.6
Example 54	52	31.7	24.1
Comparative Example 24	101	37.2	27.2
Comparative Example 25	102	38.0	29.3
Comparative Example 26	102	36.5	28.5

Table 15 (continued)

Examples and Comparative Examples	Properties of black magnetic toner		
	Magnetic properties		Blackness (L* value) (-)
	Residual magnetization		
	(10 kOe) (emu/g)	(1 kOe) (emu/g)	
Example 47	5.8	4.3	18.5
Example 48	4.1	2.9	17.9
Example 49	11.1	8.4	19.2
Example 50	4.4	3.2	19.3
Example 51	5.3	4.0	17.6
Example 52	3.7	2.8	18.2
Example 53	10.1	7.2	18.0
Example 54	4.7	3.1	19.1
Comparative Example 24	5.1	4.0	22.2
Comparative Example 25	5.1	4.0	23.6
Comparative Example 26	5.0	4.1	23.0

Table 16

Examples and Comparative Examples	Production of black magnetic toner			
	Black magnetic composite particles		Resin	
	Kind	Amount blended (part by weight)	Kind	Amount blended (part by weight)
Example 55	Example 31	45	Styrene-acryl copolymer resin	55
Example 56	Example 32	45	Styrene-acryl copolymer resin	55
Example 57	Example 33	40	Styrene-acryl copolymer resin	60
Example 58	Example 34	50	Styrene-acryl copolymer resin	50
Example 59	Example 35	45	Styrene-acryl copolymer resin	55
Example 60	Example 36	40	Styrene-acryl copolymer resin	60
Example 61	Example 37	50	Styrene-acryl copolymer resin	50
Example 62	Example 38	50	Styrene-acryl copolymer resin	50
Comparative Example 27	Comparative Example 18	45	Styrene-acryl copolymer resin	55
Comparative Example 28	Comparative Example 19	45	Styrene-acryl copolymer resin	55
Comparative Example 29	Comparative Example 20	45	Styrene-acryl copolymer resin	55

Table 16 (continued)

Examples and Comparative Examples	Properties of black magnetic toner			
	Average particle size (μm)	Dispers-ibility (-)	Fluidity index (-)	Volume resistivity (Ω•cm)
Example 55	10.0	5	76	$9.2x10^{13}$
Example 56	10.0	5	80	$2.5x10^{14}$
Example 57	10.1	4	76	$6.5x10^{13}$
Example 58	9.9	5	81	$7.8x10^{13}$
Example 59	10.1	5	80	$7.3x10^{13}$
Example 60	9.8	5	85	$3.2x10^{14}$
Example 61	10.2	5	75	$2.6x10^{14}$
Example 62	10.0	5	83	$1.4x10^{14}$
Comparative Example 27	10.2	2	60	$1.8x10^{12}$
Comparative Example 28	10.4	2	59	$3.1x10^{12}$
Comparative Example 29	10.2	2	60	$3.4x10^{12}$

Table 16 (continued)

Examples and Comparative Examples	Properties of black magnetic toner		
	Magnetic properties		
	Coercive force (Oe)	Saturation magnetization	
		(10 kOe) (emu/g)	(1 kOe) (emu/g)
Example 55	96	36.5	27.4
Example 56	61	33.8	26.5
Example 57	321	34.4	23.2
Example 58	58	32.6	22.4
Example 59	102	32.0	23.4
Example 60	66	29.4	22.1
Example 61	318	33.4	25.6
Example 62	51	31.6	23.4
Comparative Example 27	101	38.2	27.8
Comparative Example 28	102	38.2	29.3
Comparative Example 29	100	36.7	28.5

Table 16 (continued)

Examples and Comparative Examples	Properties of black magnetic toner		
	Magnetic properties		Blackness
	Residual magnetization		(L* value)
	(10 kOe) (emu/g)	(1 kOe) (emu/g)	(-)
Example 55	5.8	4.3	18.4
Example 56	4.1	2.8	17.9
Example 57	11.4	8.6	19.3
Example 58	4.5	3.3	18.8
Example 59	5.3	4.1	17.2
Example 60	3.7	2.8	17.9
Example 61	8.6	6.4	18.3
Example 62	4.3	3.1	18.6
Comparative Example 27	5.9	4.6	23.3
Comparative Example 28	5.3	4.1	22.8
Comparative Example 29	5.0	3.9	22.2

Table 17

Examples and Comparative Examples	Production of black magnetic toner			
	Black magnetic particles		Resin	
	Kind	Amount blended (part by weight)	Kind	Amount blended (part by weight)
Example 63	Example 39	45	Styrene-acryl copolymer resin	55
Example 64	Example 40	45	Styrene-acryl copolymer resin	55
Example 65	Example 41	40	Styrene-acryl copolymer resin	60
Example 66	Example 42	50	Styrene-acryl copolymer resin	50
Example 67	Example 43	45	Styrene-acryl copolymer resin	55
Example 68	Example 44	40	Styrene-acryl copolymer resin	60
Example 69	Example 45	50	Styrene-acryl copolymer resin	50
Example 70	Example 46	50	Styrene-acryl copolymer resin	50
Comparative Example 30	Comparative Example 21	45	Styrene-acryl copolymer resin	55
Comparative Example 31	Comparative Example 22	45	Styrene-acryl copolymer resin	55
Comparative Example 32	Comparative Example 23	45	Styrene-acryl copolymer resin	55

Table 17 (continued)

Examples and Comparative Examples	Properties of black magnetic toner			
	Average particle size (μm)	Dispersibility (-)	Fluidity index (-)	Volume resistivity (Ω•cm)
Example 63	10.1	5	75	8.6×10^{13}
Example 64	9.8	5	78	2.1×10^{14}
Example 65	10.2	4	72	6.5×10^{13}
Example 66	9.9	5	80	7.3×10^{13}
Example 67	10.3	5	80	7.1×10^{13}
Example 68	10.0	5	82	3.2×10^{14}
Example 69	9.6	5	79	1.6×10^{14}
Example 70	10.0	5	83	2.1×10^{14}
Comparative Example 30	9.8	2	59	1.2×10^{12}
Comparative Example 31	9.9	2	57	1.4×10^{12}
Comparative Example 32	10.0	2	57	3.2×10^{12}

Table 17 (continued)

Examples and Comparative Examples	Properties of black magnetic toner		
	Magnetic properties		
	Coercive force (Oe)	Saturation magnetization (10 kOe) (emu/g)	Saturation magnetization (1 kOe) (emu/g)
Example 63	98	36.9	27.3
Example 64	62	33.8	26.2
Example 65	308	34.9	23.1
Example 66	58	32.6	22.6
Example 67	101	32.6	23.1
Example 68	64	32.6	22.6
Example 69	313	33.2	24.2
Example 70	56	32.1	23.1
Comparative Example 30	102	38.6	27.3
Comparative Example 31	103	37.9	25.6
Comparative Example 32	101	37.1	28.3

Table 17 (continued)

Examples and Comparative Examples	Properties of black magnetic toner		
	Magnetic properties		Blackness (L* value) (-)
	Residual magnetization		
	(10 kOe) (emu/g)	(1 kOe) (emu/g)	
Example 63	5.6	4.2	18.6
Example 64	3.6	2.8	17.8
Example 65	12.1	8.4	19.0
Example 66	3.6	3.1	18.6
Example 67	5.1	3.9	17.4
Example 68	3.8	2.5	18.0
Example 69	10.6	5.2	18.3
Example 70	4.3	3.4	18.9
Comparative Example 30	5.8	4.3	23.2
Comparative Example 31	5.3	4.2	23.5
Comparative Example 32	5.0	4.0	23.1

Table 18

Examples and Comparative Examples	Kind of particles to be treated	Production of black magnetic composite particles — Coating step with fluoroalkylsilane compound — Fluoroalkylsilane compound: Kind	Amount added (part by weight)
Example 71	Core particles 1	Tridecafluorooctyl trimethoxysilane	2.0
Example 72	Core particles 2	Heptadecafluorodecyl trimethoxysilane	4.0
Example 73	Core particles 3	Trifluoropropyl trimethoxysilane	3.0
Example 74	Core particles 4	Tridecafluorooctyl trimethoxysilane	1.0
Example 75	Core particles 5	Tridecafluorooctyl trimethoxysilane	6.0
Example 76	Core particles 6	Heptadecafluorodecyl trimethoxysilane	4.0
Example 77	Core particles 7	Trifluoropropyl trimethoxysilane	0.5
Example 78	Core particles 8	Tridecafluorooctyl trimethoxysilane	1.5
Comparative Example 33	Core particles 1	Tridecafluorooctyl trimethoxysilane	2.0
Comparative Example 34	Core particles 1	Tridecafluorooctyl trimethoxysilane	3.0
Comparative Example 35	Core particles 1	Tridecafluorooctyl trimethoxysilane	0.005

Table 18 (continued)

Examples and Comparative Examples	Production of black magnetic composite particles		
	Coating step with fluoroalkylsilane compound		
	Edge runner treatment		Coating amount (calculated as Si) (wt. %)
	Linear load (Kg/cm)	Time (min)	
Example 71	60	30	0.13
Example 72	45	25	0.20
Example 73	30	40	0.47
Example 74	75	45	0.07
Example 75	60	30	0.39
Example 76	60	20	0.21
Example 77	30	45	0.08
Example 78	30	60	0.10
Comparative Example 33	60	30	0.13
Comparative Example 34	60	30	0.21
Comparative Example 35	60	30	3.0×10^{-4}

Table 18 (continued)

Examples and Comparative Examples	Production of black magnetic composite particles	
	Adhering step of carbon black fine particles	
	Carbon black fine particles	
	Kind	Amount added (part by weight)
Example 71	A	8.0
Example 72	A	6.0
Example 73	B	5.0
Example 74	C	13.0
Example 75	A	10.0
Example 76	A	10.0
Example 77	B	18.0
Example 78	C	16.0
Comparative Example 33	-	-
Comparative Example 34	A	0.01
Comparative Example 35	B	5.0

Table 18 (continued)

Examples and Comparative Examples	Production of black magnetic composite particles		
	Adhering step of carbon black fine particles		
	Edge runner treatment		Amount adhered (calculated as C) (wt. %)
	Linear load (Kg/cm)	Time (min)	
Example 71	60	30	7.41
Example 72	30	45	5.69
Example 73	60	30	4.79
Example 74	30	45	11.53
Example 75	60	25	9.00
Example 76	30	60	9.10
Example 77	60	45	15.17
Example 78	30	45	13.82
Comparative Example 33	-	-	-
Comparative Example 34	60	30	0.01
Comparative Example 35	60	30	4.75

Table 19

Examples and Comparative Examples	Properties of black magnetic composite particles			
	Average particle size (µm)	Aspect ratio (-)	Geometrical standard deviation (-)	BET specific surface area (m^2/g)
Example 71	0.29	-	1.53	6.3
Example 72	0.23	-	1.33	12.8
Example 73	0.40	8.1:1	1.52	26.8
Example 74	0.23	-	1.43	14.6
Example 75	0.29	-	1.53	15.3
Example 76	0.23	-	1.33	14.8
Example 77	0.40	8.1:1	1.51	28.8
Example 78	0.23	-	1.43	13.4
Comparative Example 33	0.28	-	1.52	10.0
Comparative Example 34	0.29	-	1.52	9.8
Comparative Example 35	0.29	-	1.52	13.6

Table 19 (continued)

Examples and Comparative Examples	Properties of black magnetic composite particles		
	Magnetic properties		
	Coercive force (Oe)	Saturation magnetization (10 kOe) (emu/g)	Residual magnetization (10 kOe) (emu/g)
Example 71	108	81.5	11.7
Example 72	68	72.4	6.5
Example 73	343	74.6	25.3
Example 74	58	64.3	6.1
Example 75	107	73.2	10.0
Example 76	67	73.6	6.5
Example 77	340	78.1	26.3
Example 78	57	63.2	6.5
Comparative Example 33	103	83.3	9.9
Comparative Example 34	103	84.1	9.8
Comparative Example 35	103	83.3	10.2

Table 19 (continued)

Examples and Comparative Examples	Properties of black magnetic composite particles		
	Fluidity index (-)	Blackness (L* value) (-)	Carbon black desorption percentage (%)
Example 71	47	16.4	6.1
Example 72	48	16.8	7.4
Example 73	50	17.3	8.2
Example 74	46	17.8	5.6
Example 75	51	16.5	4.3
Example 76	52	16.3	4.1
Example 77	53	17.6	3.8
Example 78	52	17.8	4.8
Comparative Example 33	38	20.6	79.1
Comparative Example 34	38	20.8	28.7
Comparative Example 35	37	20.3	53.4

Table 20

Examples and Comparative Examples	Production of black magnetic toner			
	Black magnetic particles		Resin	
	Kind	Amount blended (part by weight)	Kind	Amount blended (part by weight)
Example 79	Example 71	45	Styrene-acryl copolymer resin	55
Example 80	Example 72	45	Styrene-acryl copolymer resin	55
Example 81	Example 73	40	Styrene-acryl copolymer resin	60
Example 82	Example 74	50	Styrene-acryl copolymer resin	50
Example 83	Example 75	45	Styrene-acryl copolymer resin	55
Example 84	Example 76	40	Styrene-acryl copolymer resin	60
Example 85	Example 77	50	Styrene-acryl copolymer resin	50
Example 86	Example 78	50	Styrene-acryl copolymer resin	50
Comparative Example 36	Comparative Example 33	45	Styrene-acryl copolymer resin	55
Comparative Example 37	Comparative Example 34	45	Styrene-acryl copolymer resin	55
Comparative Example 38	Comparative Example 35	45	Styrene-acryl copolymer resin	55

Table 20 (continued)

Examples and Comparative Examples	Properties of black magnetic toner			
	Average particle size (μm)	Dispers-ibility (-)	Fluidity index (-)	Volume resistivity (Ω•cm)
Example 79	10.0	5	76	8.1×10^{13}
Example 80	9.8	4	81	2.1×10^{14}
Example 81	10.1	4	73	6.5×10^{13}
Example 82	10.3	5	82	9.2×10^{13}
Example 83	10.2	5	85	5.4×10^{13}
Example 84	10.0	5	86	3.6×10^{14}
Example 85	9.9	5	83	2.6×10^{14}
Example 86	9.8	5	84	3.8×10^{14}
Comparative Example 36	10.1	2	57	1.3×10^{12}
Comparative Example 37	10.3	2	56	2.4×10^{12}
Comparative Example 38	10.1	2	56	6.8×10^{12}

Table 20 (continued)

Examples and Comparative Examples	Properties of black magnetic toner		
	Magnetic properties		
	Coercive force (Oe)	Saturation magnetization	
		(10 kOe) (emu/g)	(1 kOe) (emu/g)
Example 79	100	36.9	27.0
Example 80	63	34.8	26.4
Example 81	315	34.3	22.9
Example 82	58	31.6	22.6
Example 83	101	32.1	23.3
Example 84	61	32.8	22.2
Example 85	318	32.6	24.1
Example 86	55	32.1	23.0
Comparative Example 36	101	38.4	27.3
Comparative Example 37	100	38.0	25.3
Comparative Example 38	101	37.1	27.2

Table 20 (continued)

Examples and Comparative Examples	Properties of black magnetic toner		
	Magnetic properties		Blackness (L* value) (-)
	Residual magnetization		
	(10 kOe) (emu/g)	(1 kOe) (emu/g)	
Example 79	5.7	4.1	18.5
Example 80	3.7	2.8	17.6
Example 81	12.3	8.3	18.8
Example 82	3.8	3.0	18.6
Example 83	5.6	3.4	17.2
Example 84	3.6	2.1	18.3
Example 85	9.8	5.3	17.3
Example 86	3.7	3.2	17.3
Comparative Example 36	5.4	4.3	23.4
Comparative Example 37	5.3	4.5	23.2
Comparative Example 38	5.0	4.0	22.2

Claims

1. Black magnetic composite particles for a black magnetic toner, comprising:

(a) magnetic iron oxide particles having an average particle diameter of from 0.055 to 0.95 μm;
(b) a coating on the surface of said magnetic iron oxide particles, comprising at least one organosilicon compound selected from:

(1) organosilane compounds obtainabl by drying or heat-tr ating alkoxysilan compounds,
(2) polysiloxanes or modified polysiloxanes, and
(3) fluoroalkyl organosilane compounds obtainable by drying or heat-treating fluoroalkylsilane compounds; and

(c) carbon black fine particles adhered on at least a part of said coating, which hav a particl siz of from

0.002 to 0.05 μm and which are present in an amount of from 1 to 25 parts by weight per 100 parts by weight of said magn tic iron oxide particles.

2. Particles according to claim 1, wherein said magnetic iron oxide particles have a coat on at least a part of th surface thereof, which comprises at least one hydroxide or oxide selected from hydroxides of aluminum, oxides of aluminum, hydroxides of silicon and oxides of silicon in an amount of from 0.01 to 50 % by weight, calculated as Al and/or SiO_2, based on the total weight of the magnetic iron oxide particles.

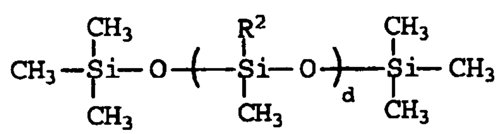
3. Particles according to claim 1 or 2, wherein said alkoxysilane compound is represented by the general formula (I):

$$R^1{}_aSiX_{4-a} \qquad (I)$$

wherein R^1 is C_6H_5-, $(CH_3)_2CHCH_2$- or n-C_bH_{2b+1}- (wherein b is an integer of from 1 to 18); X is CH_3O- or C_2H_5O-; and a is an integer of from 0 to 3.

4. Particles according to claim 3, wherein said alkoxysilane compound is methyl triethoxysilane, dimethyl diethoxysilane, tetraethoxysilane, phenyl triethoxysilane, diphenyl diethoxysilane, methyl trimethoxysilane, dimethyl dimethoxysilane, tetramethoxysilane, phenyl trimethoxysilane, diphenyl dimethoxysilane, isobutyl trimethoxysilane or decyl trimethoxysilane.

5. Particles according to any one of the preceding claims, wherein said polysiloxanes are represented by the general formula (II):



(II)

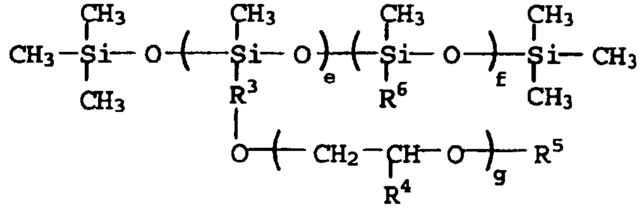
wherein R^2 is H- or CH_3-, and d is an integer of 15 to 450.

6. Particles according to claim 5, wherein said polysiloxanes have methyl hydrogen siloxane units.

7. Particles according to any one of the preceding claims, wherein said modified polysiloxanes are selected from:

(A) polysiloxanes modified with at least one polyether and/or polyester and/or epoxy compound, and
(B) polysiloxanes whose molecular terminal is modified with at least one group selected from carboxylic acid, alcohol and hydroxyl groups.

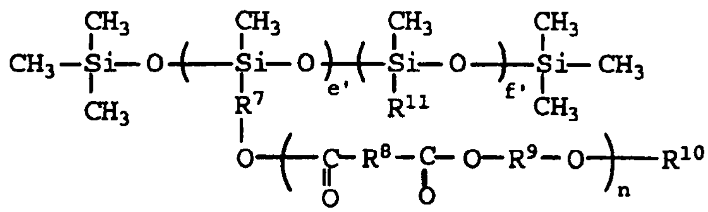
8. Particles according to claim 7, wherein said polysiloxanes (A) are represented by the general formula (III), (IV) or (V):



(III)

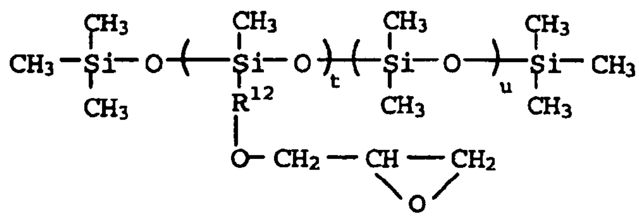
wherein R^3 is $-(-CH_2-)_h-$; R^4 is $-(-CH_2-)_i-CH_3$; R^5 is -OH, -COOH, $-CH=CH_2$, $-C(CH_3)=CH_2$ or $-(-CH_2-)_j-CH_3$; R^6 is $-(-CH_2-)_k-CH_3$; g and h are integers of from 1 to 15; i, j and k are integers of from 0 to 15; e is an integer of from

1 to 50; and f is an integer of from 1 to 300;



(IV)

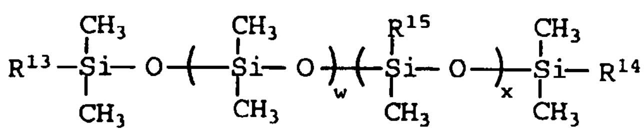
wherein R^7, R^8 and R^9 are $-(-CH_2-)_q-$ and may be the same or different; R^{10} is -OH, -COOH, $-CH=CH_2$, $-C(CH_3)=CH_2$ or $-(-CH_2-)_r-CH_3$; R^{11} is $-(-CH_2-)_s-CH_3$; n and q are integers of from 1 to 15; r and s are integers of from 0 to 15; e' is an integer of from 1 to 50; and f' is an integer of from 1 to 300; or



(V)

wherein R^{12} is $-(-CH_2-)_v-$; v is an integer of from 1 to 15; t is an integer of from 1 to 50; and u is an integer of from 1 to 300.

9. Particles according to claim 7 or 8, wherein said polysiloxanes (B) are represented by the general formula (VI):



(VI)

wherein R^{13} and R^{14} are -OH, $R^{16}OH$ or $R^{17}COOH$ and may be the same or different; R^{15} is $-CH_3$ or $-C_6H_5$; R^{16} and R^{17} are $-(-CH_2-)_y-$; y is an integer of from 1 to 15; w is an integer of from 1 to 200; and x is an integer of from 0 to 100.

10. Particles according to any one of the preceding claims, wherein said fluoroalkylsilane compounds are represented by the general formula (VII):

$$CF_3(CF_2)_zCH_2CH_2(R^{18})_{a'}SiX_{4-a'} \qquad \text{(VII)}$$

wherein R^{18} is CH_3-, C_2H_5-, CH_3O- or C_2H_5O-; X is CH_3O- or C_2H_5O-; and z is an integer of from 0 to 15; and a' is an integer of from 0 to 3.

11. Particles according to any one of the preceding claims, wh rein the amount of said coating organosilicon compound(s) is from 0.02 to 5.0 % by weight, calculated as Si, based on the total weight of the organosilicon compound(s) and said magnetic iron oxide particles.

12. Particles according to any one of the preceding claims, which have an average particl diameter of from 0.06 to

1.0 μm

13. Particles according to any one of the pr ceding claims, which hav a geometrical standard deviation of particle siz s of from 1.01 to 2.0.

14. Particles according to any one of the preceding claims, which have a BET specific surface area value of from 1 to 200 m^2/g.

15. Particles according to any one of the preceding claims, which have a flowability index of from 45 to 80.

16. Particles according to any one of the preceding claims, which have a blackness (L* value) of from 15 to 20.

17. Black magnetic toner comprising said black magnetic composite particles according to any one of the preceding claims.

18. Toner according to claim 17, which comprises from 50 to 900 parts by weight of a binder resin per 100 parts by weight of said black magnetic composite particles.

19. Toner according to claim 17 or 18, which has an average particle size of from 3 to 15 μm.

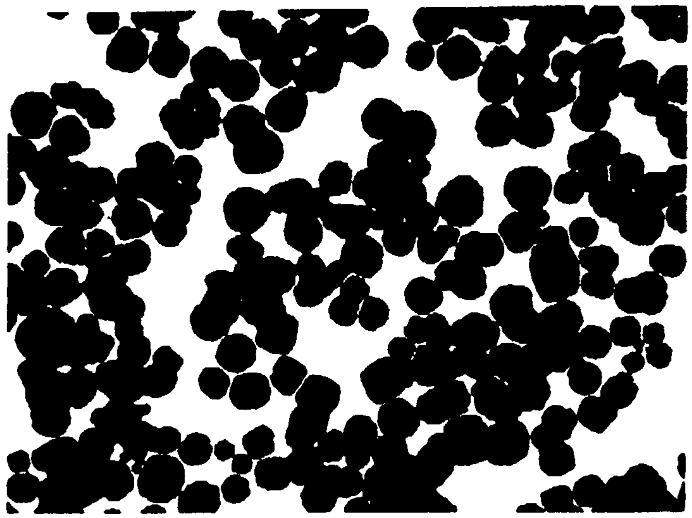
20. Toner according to any one of claims 17 to 19, which has a flowability index of from 70 to 100.

21. Toner according to any one of claims 17 to 20, which has a blackness (L* value) of from 15 to 20.

22. Toner according to any one of claims 17 to 21, which has a volume resistivity of from 1.0×10^{13} to 1.0×10^{15} Ω.

23. A method for production of a black magnetic toner, which method comprises mixing black magnetic composite particles according to any one of claims 1 to 16 with a binder resin and processing the resulting mixture thereby to form the toner.

FIG.1



(×20000)

FIG.2

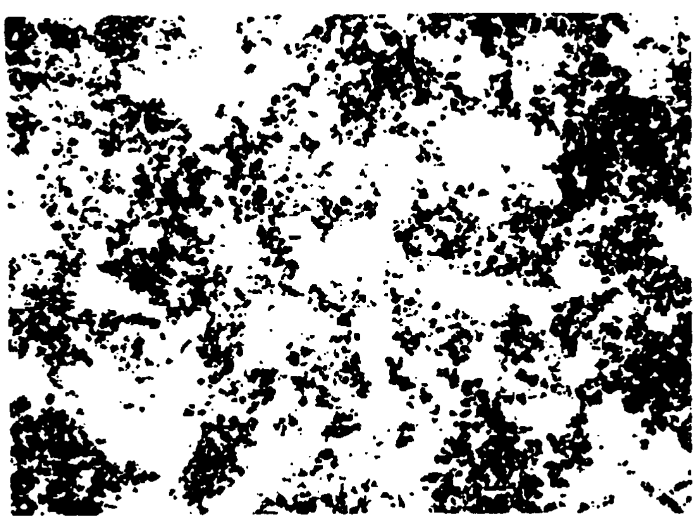


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FIG.3

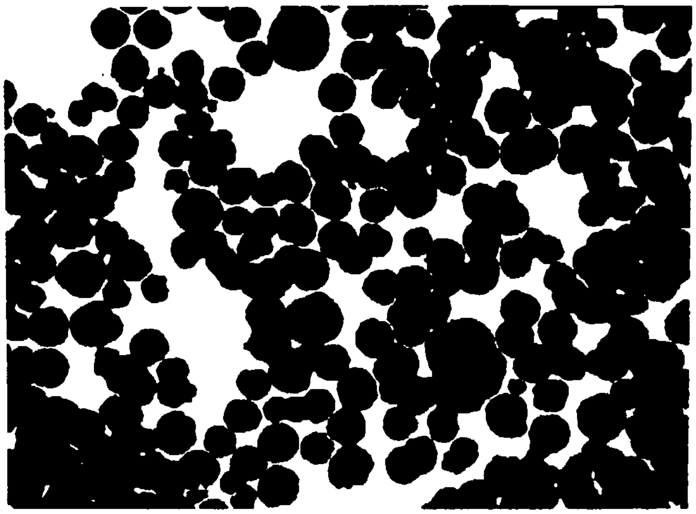

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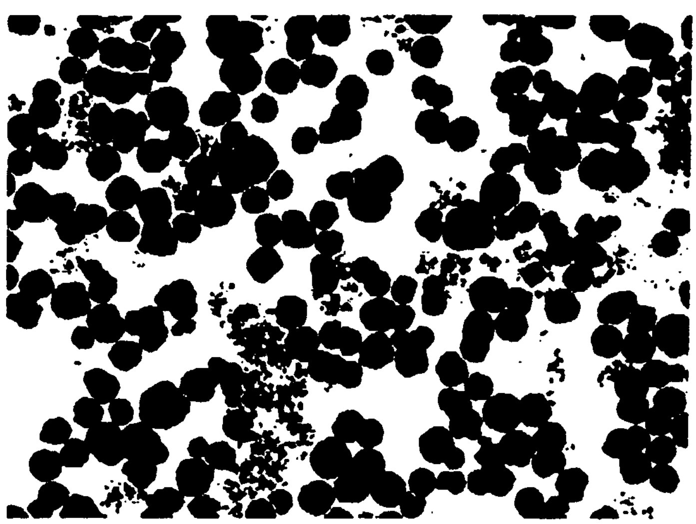
FIG.4



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